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Edwin Bradley Deyton
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To the Graduate Council:

I am submitting herewith a thesis written by Edwin Bradley Deyton entitled "Characterizing Episodic Stream Acidity During Stormflow in the Great Smoky Mountains National Park." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

John S. Schwartz, Major Professor

We have read this thesis and recommend its acceptance:

R. Bruce Robinson, Randall W. Gentry

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Carolyn R. Hodges
Vice Provost and Dean of
the Graduate School

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Characterizing Episodic Stream Acidity During Stormflow in the Great Smoky Mountains National Park

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Edwin Bradley Deyton
August 2007

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Abstract

Episodic stream acidification occurs as storm events temporarily reduce acid neutralizing capacity (ANC) and pH. Stream acidification is suspected to have damaging effects on the health of aquatic ecosystems and biota. The objectives of this research are to 1) characterize stream baseflow and stormflow chemistries in three watersheds in the Great Smoky Mountains National Park (GRSM), 2) understand potential mechanisms responsible for episodic acidification, and 3) understand the relationship between storm event magnitude, antecedent soil moisture condition, and the stream's pH response. Three remote, forested, high-elevation streams (Middle Prong, Ramsey Prong, and Eagle Rocks Prong) were selected in the Middle Prong of the Little Pigeon River Watershed. Multi-parameter data sondes were installed at each site to record continuous stream data. Autosamplers were set up in connection with the sondes to collect samples during storm events. Stormflow, baseflow, and precipitation samples were analyzed for pH, ANC, and a broad spectrum of cations and anions that contribute to the ion balance.

During stormflow, ANC and pH depressions were observed for all storms at each study site. Sulfate, nitrate, and organic acid concentrations increased during each storm. Base cation concentrations generally increased during stormflow at Middle and Ramsey Prongs, but diluted occasionally on Eagle Rocks Prong. The relative changes in ion concentrations were used to determine which ions (acids) were most responsible for ANC depression. ANC contribution analysis indicates acid deposition may be the primary cause of episodic acidification, but it appears organic acids and cation dilution may also contribute. Pyritic geology is also suspected to contribute to baseflow and stormflow acidity in the Eagle Rocks Prong. Data exploration indicates large storms preceded by

long, dry periods cause the largest pH depressions. It appears stream acidification may be driven by acid deposition, but additional inputs from varying vegetation and geology create unique and complex response to the observed stream acidification.

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NOTE: This paper is being submitted as a manuscript to a scientific journal. All appendices are additional research information that was not deemed publishable, but was included for supplementary documentation of findings.

INTRODUCTION

Episodic acidification of surface water, defined as the short term reduction of pH and acid neutralizing capacity (ANC) resulting from a hydrologic event, is a ubiquitous phenomenon observed in the eastern United States, Canada, and northern Europe (Wigington et al. 1996b). The cause of episodic acidification is a complex interaction of natural and anthropogenic processes (Kahl et al. 1992). Episode chemistry is influenced by the storm event, the hydrologic flowpaths operating during the event, the acid-base reactions occurring in the soil, and the antecedent moisture conditions of the soil (Tranter et al. 1994). The severity of each episode may vary spatially and seasonally (Wigington et al. 1990). Previous studies have shown that streams and lakes may experience pH <5.0 and ANC <0 during acidic episodes (Wigington et al. 1996b). Episodic stream acidification has been shown to have damaging effects on aquatic ecosystems and biota (Potter et al. 1988, Carline RF 1992). Episodic acidification has caused adverse impacts to water quality and aquatic biota in the Great Smoky Mountains National Park (GRSM) (Roby 2005, Jackson 2006). There is concern from the GRSM resource managers that continued episodic events may extirpate native trout, salamanders, and other aquatic life in streams (Moore 2007).

High elevation watersheds are particularly sensitive to episodic acidification (Deviney et al. 2006). In the eastern United States, most acidic streams are located in small, high elevation, forested watersheds in the base-poor bedrock of the Appalachian

Mountains (Herlihy et al. 1993). A study of upland watersheds found that catchments with higher elevations and smaller areas were more likely to be susceptible to acidification (Deviney et al. 2006). Acid deposition rates tend to be higher in the mountains due to dry deposition, cloud water deposition, and increased orographic acid rain (Lovett and Kinsman 1990). Headwater streams are typically more sensitive to acid deposition because of their thin soils, steep slopes, high precipitation, and base-poor soils that offer limited buffering capacity (Sullivan et al. 2007).

Several regional studies have identified acid deposition as the dominant mechanism for acidic episodes in the Mid-Atlantic and Southern Appalachians (Herlihy et al. 1991, Herlihy et al. 1993). Organic acids are a possible source of acidity, but are not likely to be a dominant source in streams with low dissolved organic carbon (Herlihy et al. 1993). Additionally, Anakeesta pyritic geology has been identified as a natural source of acid in the GRSM (Huckabee et al. 1975). Anakeesta is relatively non-reactive until exposed to air and water, whereupon it oxidizes to release acid and heavy metals to adjacent bodies of water. Multiple studies have cited the damaging effects resulting from Anakeesta leachates impacting aquatic species, particularly in road construction areas within the GRSM (Huckabee et al. 1975, Bacon and Maas 1979). Lastly, increased streamflow during storm events causes a dilution of most solutes (Kahl et al. 1992). The dilution of base cation concentration is an acidifying mechanism that commonly depresses ANC during high stream flow.

The hydrologic flowpath of stream water may control which factors contribute to acidification. Baseflow water derives from the lower mineral soil that contains water with higher ANC values. During stormflow, more water is routed through the upper soil

layers which are more acidic due to acid deposition or other natural processes, such as the flushing of organic acids or base cation dilution (Wellington and Driscoll 2004). The stormwater has less time to react with base cations in the soil and is generally more acidic upon reaching streamflow (Wigington et al. 1996b). Soil macropores may also play an important role in shallow groundwater flow because they allow acid rain water to reach the stream quickly, thus minimizing the potential for buffering (Potter et al. 1988).

There is a need to understand the anthropogenic and natural acidification processes that may occur in the GRSM. The GRSM receives among the highest rates of atmospheric deposition of acids in the U.S. (Shubzda J. 1995), which is related to regional coal-fired power plants and vehicular traffic (Baird and Cann 2005). There are also previously identified natural sources of acid: Anakeesta geology and organic acids (Huckabee et al. 1975, Cook et al. 1994). Additionally, there is a need to understand the variability of episodic events in the GRSM. Previous work in the lower elevations of the Middle Prong of the Little Pigeon River watershed, in the GRSM, shows the potential for a variable pH and ANC response between different sites and storm events (Roby 2005).

The objectives of this study are to 1) characterize stream chemistry during episodic stormflow events in comparison with baseflow water chemistry, 2) understand responsible acidification mechanisms in three high elevation watersheds, and 3) understand the relationship between storm event magnitude, antecedent soil moisture condition, and the stream's pH response. We hypothesize that acid deposition is the dominant process causing acidification in streams within the GRSM. This hypothesis is based on low DOC concentrations at each of the stream study sites, which limits the potential for organic acid influence. Pyritic geology is not significantly present (3% by

area) in the Middle Prong of the Little Pigeon watershed, thus is not likely a primary source of acid, but may contribute to acidity.

METHODS:

Study Area:

The Middle Prong of the Little Pigeon (MPLP) watershed is defined as the 117.4 km^2 area that drains to the portion of the Middle Prong of the Little Pigeon River within the boundaries of the GRSM. The MPLP watershed terrain is characterized by sharp crested ridges with steep sides, separated by deep valleys in between ridges. The average slope of the MPLP watershed is 25.4%. The vegetation is composed of deciduous and broadleaf trees at low-to-middle elevations, but also contains evergreen coniferous forests at higher elevations. The watershed geology is characterized by sandstone, siltstone, shale, and slate (King 1968). The base-poor geology contributes to limited buffering capacity and vulnerability to acid inputs. The soils are thin and consist of rocky, sandy loams. The climate is perhumid mesothermal with seasonal temperature variations and precipitation distributed throughout the year. The GRSM average annual temperature is 13.2 ^{o}C and the mean precipitation is 141 cm. The Alum Cave Bluffs Parking Area station, which is more representative of the MPLR study site, receives an average of 200 cm precipitation with an average temperature of 9.9 ^{o}C (Busing 2005).

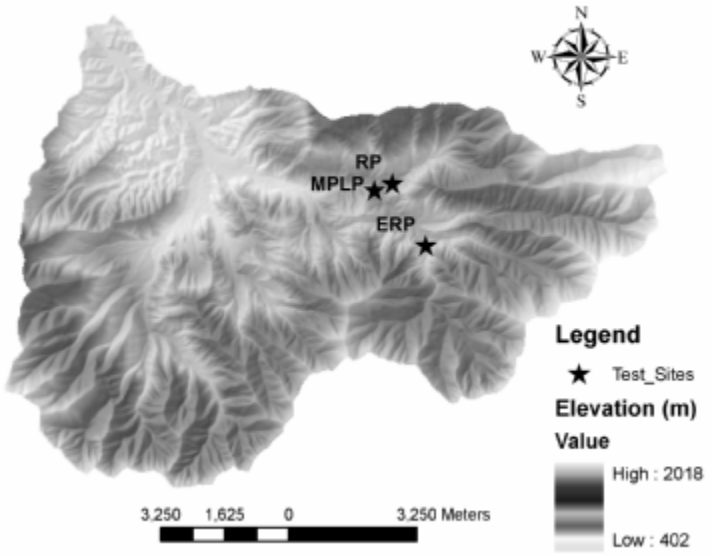

Figure 1. Map of the MPLP study area in the GRSM

Three study sites were selected within the MPLP watershed to conduct water quality monitoring: Middle Prong of the Little Pigeon River, Ramsey Prong, and Eagle Rocks Prong. Ramsey Prong and Eagle Rocks Prong are tributaries of the Middle Prong of the Little Pigeon River. The Middle Prong is a fifth-order mountain stream, while Ramsey Prong and Eagle Rocks Prong are fourth-order mountains streams. The drainage areas are 38.7, 10.3, and 10.5 km^2, respectively.

The MPLP study sites are remote and removed from any potential impacts from physical anthropogenic disturbance. All sites were at a minimum of 2.4 km from any roads and are accessible only by hiking trails and wading sections of river. The only anthropogenic impacts are in the form of atmospheric deposition of acid across the watershed.

Study Design:

Sites M1, M2, and M3 were stationed along the Middle Prong, Ramsey Prong, and Eagle Rocks Prong, respectively. Study sites were established on Ramsey Prong and Eagle Rocks Prong as each stream once supported native brook trout (*Salvelinus fontinalis*) populations, but no longer does. The Middle Prong was chosen because it collects Ramsey and Eagle Rocks Prong, but still supports a trout population. The Middle Prong additionally drains 17.9 km^2 of other sub-watersheds within the MPLP watershed. The elevations for M1, M2, and M3 are 823, 877, and 966 m, respectively.

The study sites were set up to monitor streamwater quality. Each site was equipped with a YSI 6920 multi-parameter sonde to record continuous 15-min data of pH, depth, conductivity, turbidity, and temperature. ISCO 6712 composite samplers were installed to collect stream samples during storm events. Storm sampling was triggered by an incremental depth increase or pH decrease, as measured by the sondes. Stream samples were collected every 45 minutes for the first six hours, then every two hours for the next 30 hours to collect representative samples of the entire storm event hydrograph. To determine baseflow stream chemistry, grab samples were taken at the beginning of the month and when conditions permitted, prior to storm events.

Precipitation samples were collected monthly and/or after each storm event at the sites. Bulk throughfall precipitation was collected in buckets with eight-inch plastic funnels. Throughfall precipitation permitted an estimation of the wet and dry acid deposition in the MPLP watershed.

Comparisons were performed to evaluate seasonal differences in stream chemistry. The seasons were separated into dormant and transpiring, or leaf "on" and "off," seasons to allow comparison of the stream ion concentrations with respect to seasonal vegetative demand. The seasons were separated by the spring frost-free date of April 15, and October 15 represented the onset of plant dormancy (NOAA http://www.ncdc.noaa.gov/oa/climate/freezefrost/frostfreemaps.html).

Chemical Analysis:

All storm samples, grab samples, and precipitation samples were collected in LDPE plastic bottles that had been triple rinsed in the lab with de-ionized water. Grab and precipitation samples were also triple rinsed in the field with sample water. All samples were analyzed for pH, ANC, and conductivity using a ManTech ®autotitrator. Major cations and trace metals (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, Al^{n+}, Cu, Fe, Mn, Si, Zn) were analyzed using a Thermo-Electron ® inductively coupled plasma (ICP) spectrometer. Major anions (SO_4^{2-}, NO_3^{-}, Cl^{-}) and ammonia (NH_4^{+}) were measured using a Dionex ® ion chromatograph (IC).

All laboratory test procedures were conducted in accordance with published methods as described in Table 1. Each test procedure included QA/QC checks in the form of spikes, duplicates, blanks, and known samples. The QA/QC laboratory results indicate a high degree of reliability due to diligent monitoring. A formal QA/QC report is prepared annually for the GRSM.

Table 1. Analytical procedures performed for chemical analyses

Analysis	Procedure	Equipment	Method
pH	Potentiometric	PC-Titration Plus	EPA Method 150.1
Conductivity	Potentiometric	PC-Titration Plus	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus	Automated Gran Titration for low ionic strength waters as in Hillman et al. 1986
Anions	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Cations, Metals	Inductively Coupled Plasma Spectrometry	Thermo-Elemental Iris Intrepid II ICP	EPA Method 6010B & 6010C

ANC Ion Contribution Analysis:

The baseflow, stormflow, and precipitation chemistry were analyzed from March 2006 through May 2007, with a total of 15 episodes collected. The acid-base chemistry was evaluated prior to and throughout each storm. Baseflow ANC and storm event minimum ANC were used as reference points to evaluate the maximum change in acidity associated with a storm event. ANC in acidic waters may be calculated based on the concentration of bicarbonate (HCO_3^-) and proton (H^+) or by manipulation of the ion balance (μeq/L):

where:

$$ANC = [HCO_3^-] - [H^+]$$

or:

$$ANC = \sum C_B - [SO_4^{2-}] - [NO_3^-] - [Cl^-]$$

Similar to the modified Molot (1989) version used by Hyer et al. (1995), the change in concentration of sulfate, nitrate, chloride, and the sum of base cations (ΣC_B) was used to determine the relative contribution of each quantity to the total ANC change. This approach is also consistent with methods used by Wellington and Driscoll (2004) to

quantify the contribution of ion concentration change to overall ANC change for storms in the Hubbard Brook Experimental Forest. Ionic contributions were estimated as follows:

$$\Delta ANC = ANC_b - ANC_e$$

$$\Delta SO_4^{2-} = \frac{SO_{4e}^{2-} - SO_{4b}^{2-}}{\Delta ANC}$$

$$\Delta NO_3^- = \frac{NO_{3e}^- - NO_{3b}^-}{\Delta ANC}$$

$$\Delta Cl^- = \frac{Cl_e^- - Cl_b^-}{\Delta ANC}$$

$$\Delta \sum C_B = \frac{\sum C_{Bb} - \sum C_{Be}}{\Delta ANC}$$

where the subscripts "b" and "e" represent baseflow and storm event minimum ANC concentrations, respectively. The change in ion concentration divided by the total ANC change yields the relative contribution of the ion to the ANC depression. A positive ratio indicates ANC loss, while a negative ratio suggests an ANC increase. The sum of ratios for each quantity should equal a value of one.

$$\frac{\Delta SO_4^{2-}}{\Delta ANC} + \frac{\Delta NO_3^-}{\Delta ANC} + \frac{\Delta Cl^-}{\Delta ANC} + \frac{\Delta \sum C_B}{\Delta ANC} = 1.0$$

As suggested by Hyer et al. (1995), deviations from unity indicate either analytical error or the presence of unmeasured ions. QA/QC monitoring shows low analytical error, thus deviation from unity was presumed to be caused by unmeasured organic acids. The relative contribution of organic acids (OA) can be estimated as the difference between unity and the sum of ion concentration ratios:

$$\frac{\Delta OA}{\Delta ANC} = 1.0 - \frac{\Delta SO_4^{2-}}{\Delta ANC} + \frac{\Delta NO_3^-}{\Delta ANC} + \frac{\Delta Cl^-}{\Delta ANC} + \frac{\Delta \sum C_B}{\Delta ANC}$$

However, the measurement of each constituent contains a certain amount of analytical uncertainty. The propagation of errors technique was applied to determine the standard deviation associated with the organic acid calculation (Mandel 1964). Standard deviations for individual ions came from repeated measurements of USGS known samples.

Data Exploration of Watershed Hydrology and Stormflow Response

The stormflow data were explored for a relationship between pH response, storm magnitude, and soil antecedent moisture condition. The pH response was based on the antecedent baseflow pH and the storm event minimum value. The storm event magnitude was inferred from the maximum flow rate. Finally, soil antecedent moisture conditions were approximated by the number of dry days preceding the event. The number of dry days was determined by examining the depth data from the sondes to distinguish when the last rain event affected stream depth.

Statistical Analysis

Average baseflow and stormflow stream parameters were compared using a pooled t-test and ANOVA, after being checked for normality. Baseflow seasonal concentrations were also compared using a pooled t-test and ANOVA. Ion contribution ratios were compared between sites using the non-parametric Mann Whitney U-test. The site ion contribution data were pooled to evaluate seasonal differences using the Mann

Whitney U-test. Non-parametric tests were chosen for the ion contribution analysis due to the limited quantity of storm data. Statistical analyses were performed in JMP 6.1 and SPSS 14.0.

RESULTS:

Characteristics of Baseflow and Streamflow Chemistry:

Chemical differences were observed between baseflow and stormflow (Table 2). ANC and pH decrease at each site during stormflow, which indicates episodic acidification is a ubiquitous process in the MPLP watershed. Average ANC declines were generally larger for M2 and M3 (22 and 18 μeq/L, respectively) than for the M1 (13 μeq/L). However, average pH declines at all sites were similar with values of 0.89, 0.92, and 0.81 pH units for M1, M2, and M3, respectively. The storm behavior shows that as

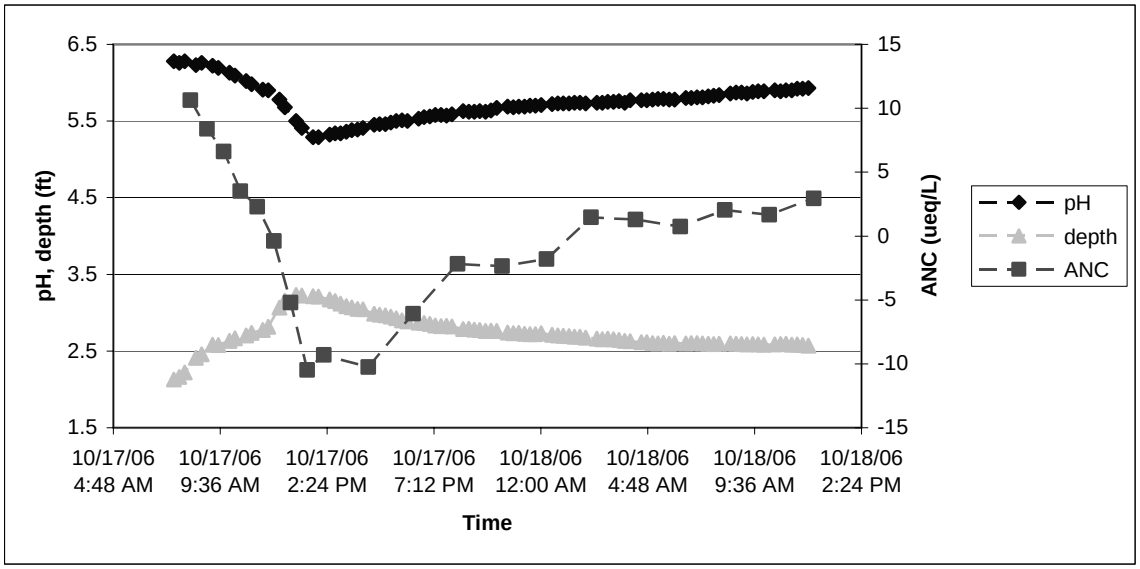

Figure 2. M1 response to storm on 10/17/06

depth increases, pH and ANC decrease; a typical response is shown in Figure 2 for a storm at M1 on 10/17/06.

Concentrations of most ions increase during stormflow; the exceptions are sodium and chloride, which generally remain constant for baseflow and stormflow (Table 2). The level of significance (p-value) for differences in mean parameter values between baseflow and stormflow is given in Table 2. The average chloride concentration differences between baseflow and stormflow are not statistically significant for any site ($p= 0.31, 0.64, 0.50$ for M1, M2, M3, respectively). Stormflow increases of sulfate were significant at each site ($p < 0.01$ for M1-3). Stormflow increases of nitrate were significant for M2 and M3 ($p= 0.01, 0.01$), but not M1 ($p= 0.17$). Although average changes in organic acid concentration were similar between sites, baseflow and stormflow differences were significant at M1 and M2 ($p< 0.01, 0.01$), but not M3 ($p= 0.10$). The method of estimating organic acids in literature is often to calculate the difference by an ion balance, but no authors present any error analysis for this technique. An error analysis based on variance in analytical measurements at these relatively low ion concentrations and propagation of errors analysis yields an estimated standard deviation in the organic acid concentration of 20.4 μeq/L.

Table 2. Baseflow and stormflow parameter data for a) M1, b) M2, and c) M3

a) M1			ANC	Cl	NO3	SO4	NH4	OA	Na	K	Mg	Ca
	Parameter	pH	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)
Baseflow	Average	5.39	5.64	11.52	43.54	45.13	0.38	11.25	27.39	9.46	25.57	54.27
n=18	Std Dev.	0.40	10.17	1.72	9.71	4.20	0.32	10.22	3.10	3.11	2.39	7.11
Stormflow	Average Peak	4.99	-12.53	12.47	50.24	60.06	2.84	27.45	26.65	18.28	30.86	67.42
n=6	Std Dev.	0.28	7.61	2.58	11.66	7.66	0.90	5.39	2.17	3.82	4.64	8.58
ANOVA	p value	0.058	<0.001**	0.311	0.166	<0.001**	<0.001**	<0.001**	0.856	<0.001**	<0.001**	0.001**

(*indicates the test is significant at p<0.05; ** indicates signficance at p<0.01)

b) M2			ANC	Cl	NO3	SO4	NH4	OA	Na	K	Mg	Ca
	Parameter	pH	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)
Baseflow	Average	5.34	3.25	11.75	35.87	39.33	0.40	10.91	26.85	11.49	18.48	44.19
n=19	Std Dev.	0.38	7.36	2.34	10.42	4.71	0.75	7.03	5.37	2.78	2.41	7.84
Stormflow	Average Peak	4.80	-9.49	12.17	55.77	51.13	4.63	23.21	27.70	18.54	26.09	70.22
n=4	Std Dev.	0.19	16.07	2.45	22.85	4.20	5.26	2.57	1.80	2.49	3.27	4.49
ANOVA	p value	0.010**	0.017*	0.639	0.010**	<0.001**	<0.001**	0.003**	0.674	<0.001**	<0.001**	<0.001**

(*indicates the test is significant at p<0.05; ** indicates signficance at p<0.01)

c) M3			ANC	Cl	NO3	SO4	NH4	OA	Na	K	Mg	Ca
	Parameter	pH	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)	(ueq/L)
Baseflow	Average	5.07	-3.87	12.15	51.40	50.01	0.90	11.36	25.95	7.96	30.40	52.79
n=18	Std Dev.	0.34	4.75	2.84	7.03	7.85	1.53	11.12	4.47	3.37	6.14	7.99
Stormflow	Average Peak	4.60	-20.65	13.32	61.54	73.35	3.83	22.05	23.02	14.12	38.47	67.06
n=5	Std Dev.	0.15	5.89	2.72	8.52	7.26	1.77	13.15	2.62	3.93	4.48	8.64
ANOVA	p value	0.008**	<0.001**	0.4950	0.010	<0.001**	0.002**	0.096	0.494	0.457	0.013*	0.003**

Higher sum of acid anion and sum of base cation concentrations were observed at each site during storms (Table 3). The observed increases in sum of base cations are significant in indicating that cation dilution does not contribute to ANC depression, on average. Total acid anion and base cation sums are generally different for each site. The sum of baseflow and stormflow acid anions is variable between sites, with Eagle Rocks having the highest concentrations. The stormflow increases in the sum of anions are by 34.8, 45.4, and 36.3% for M1, M2, and M3, respectively. The baseflow sum of cations is variable for each site, but the stormflow sums are nearly identical. The stormflow increases in sum of base cation concentrations are 24.8, 45.2, and 13.0% for M1, M2, and M3, respectively.

Table 3. Comparison of the sum of measured acid anions and base cations for baseflow and stormflow

Site	Flow Type	n (# of samples)	Σ Acid Anions (ueq/L)	Σ Acid Anions: Percent Difference	Σ Base Cations (ueq/L)	Σ Base Cations: Percent Difference
M1	Baseflow	18	111.4		117.1	
	Stormflow	6	150.2	34.8%	146.1	24.8%
M2	Baseflow	19	97.9		101.4	
	Stormflow	4	142.3	45.4%	147.2	45.2%
M3	Baseflow	18	124.9		129.7	
	Stormflow	5	170.3	36.3%	146.5	13.0%

Seasonal trends can be observed in the streamflow data (Table 4). In general, lower pH and ANC values are observed during the winter months for baseflow stream chemistry. Nitrate concentrations increase 14.4, 14.8, and 8.8 μeq/L and calcium concentrations increase by 6.9, 6.1, and 5.8 μeq/L for sites M1, M2, and M3, respectively, during the winter season. Other constituent concentrations remain generally consistent during dormant and transpiring seasons. P-values are provided for the statistical significance of seasonal concentration differences (Table 4).

Stormflow: Ionic Contributions to ANC Loss:

A total of fifteen stormflow episodes were collected from nine distinct storms. A decrease in stream ANC and pH was observed for every sampled hydrologic event. During stormflow, the concentrations of sulfate, nitrate, and organic acids generally increased while chloride concentration remained constant. The sum of base cations concentration generally increased during stormflow at M1 and M2, but occasionally diluted at M3.

The dominant mechanisms for episodic acidification varied at each site within the watershed. Table 5 provides the ΔANC, ΔpH, and ion contributions for individual storms. Box plots of the relative ionic contribution for the study sites are available in Figures 3-5.

Table 4. Seasonal baseflow concentrations for sites M1, M2, and M3 (Upper values are mean parameter value; lower values in parentheses are the parameter's standard deviation)

	Season	pH	ANC, ueq/L	Cl ueq/L	NO3-N ueq/L	SO4 ueq/L	NH4-N ueq/L	Organic Acids (ueq/L)	Na ueq/L	K ueq/L	Mg ueq/L	Ca, ueq/L	Anion Sum	Cation Sum (ueq/L)
M1	Leaves On	5.64	9.93	10.98	36.32	45.17	0.25	11.43	27.62	11.06	24.10	50.80	92.47	113.83
		(0.31)	(12.46)	(1.96)	(6.35)	(3.30)	(0.26)	(10.76)	(2.87)	(2.15)	(1.56)	(3.19)	(6.38)	(3.65)
	Leaves Off	5.15	1.35	12.06	50.76	45.09	0.52	11.06	27.16	7.85	27.05	57.73	107.90	120.31
		(0.31)	(4.81)	(1.34)	(6.54)	(5.15)	(0.33)	(10.29)	(3.47)	(3.18)	(2.18)	(8.37)	(8.03)	(13.33)
	P-value	0.004**	0.072	0.193	<0.001**	0.970	0.068	0.942	0.764	0.023*	0.005**	0.034*	<0.001**	0.178
M2	Leaves On	5.49	5.70	10.99	28.09	39.96	0.18	11.74	27.35	11.12	17.40	40.98	79.05	97.04
		(0.37)	(8.94)	(2.66)	(6.31)	(4.98)	(0.22)	(5.20)	(3.53)	(2.51)	(1.59)	(5.83)	(8.98)	(9.13)
	Leaves Off	5.21	1.04	12.43	42.86	38.77	0.59	10.24	26.41	11.82	19.45	47.08	94.07	105.34
		(0.36)	(5.10)	(1.88)	(8.18)	(4.64)	(1.00)	(8.44)	(6.80)	(3.10)	(2.69)	(8.56)	(10.98)	(16.16)
	P-value	0.116	0.175	0.189	<0.001**	0.597	0.245	0.612	0.714	0.598	0.063	0.091	0.005**	0.193
M3	Leaves On	5.31	-2.10	11.11	47.93	49.83	0.18	9.63	27.42	6.41	26.62	48.28	108.87	115.65
		(0.29)	(3.82)	(2.86)	(7.38)	(3.22)	(0.06)	(8.50)	(5.13)	(2.37)	(8.08)	(10.04)	(6.52)	(4.36)
	Leaves Off	4.87	-5.29	12.99	54.17	50.15	1.48	11.44	25.06	8.89	33.04	55.95	117.31	124.42
		(0.25)	(5.12)	(2.66)	(5.63)	(10.40)	(1.89)	(12.77)	(4.04)	(3.65)	(2.17)	(4.40)	(11.20)	(11.30)
	P-value	0.004**	0.163	0.167	0.059	0.935	0.072	0.647	0.322	0.162	0.029*	0.047*	0.074	0.494

(*indicates the test is significant at $p<0.05$; ** indicates signficance at $p<0.01$)

Table 5. pH change, ANC change, and ion contribution ratios for collected storms

Site ID	Date	ΔpH	ΔANC	ΔCl/ΔANC	ΔNO3/ΔANC	ΔSO4/ΔANC	ΔΣBC/ΔANC	ΔOA-/ΔANC
M1	06/26/06	0.77	12.3	-0.47	0.70	0.74	0.06	-0.03
	10/17/06	0.97	9.2	0.76	0.48	2.17	-3.05	0.64
	10/27/06	1.00	14.0	-0.12	0.41	-1.05	-1.44	3.19
	11/15/06	1.27	13.6	-0.06	-0.64	-0.31	1.57	0.44
	01/07/07	0.65	16.6	-0.05	-0.74	0.59	-0.86	2.06
	03/15/07	0.85	14.0	-0.04	1.64	1.17	-2.04	0.27
M2	06/26/06	0.97	18.2	-0.22	0.57	0.61	-1.13	1.17
	07/21/06	1.08	25.0	-0.12	0.83	0.85	-1.72	1.16
	03/01/07	1.22	25.0	-0.14	1.06	0.66	0.07	-0.65
	03/16/07	1.00	21.2	0.01	2.01	0.93	-1.90	-0.06
M3	04/21/06	1.2	13.7	0.02	-0.19	0.87	0.27	0.00
	10/17/06	1.27	14.5	0.70	0.14	4.40	-5.64	1.40
	01/07/07	0.74	12.6	-0.03	0.25	1.22	0.39	-0.83
	03/01/07	1.05	26.3	0.01	0.03	0.51	0.53	-0.09
	03/16/07	0.83	23.7	-0.03	0.50	1.01	0.55	-0.62

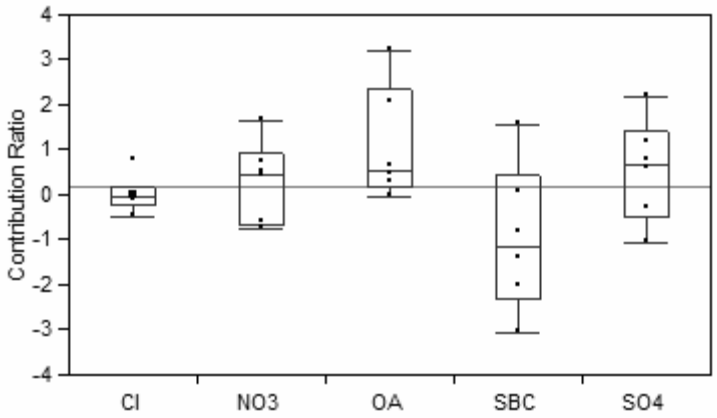

Figure 3. Box Plot of relative ion contribution ratios for M1 storms

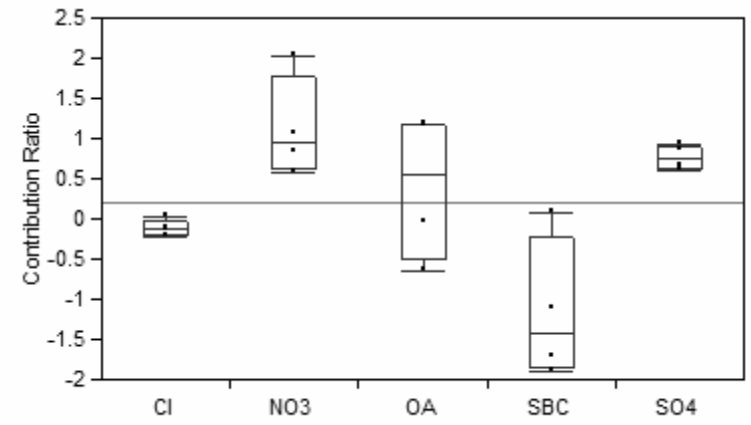

Figure 4. Box Plot of relative ion contribution ratios for M2 storms

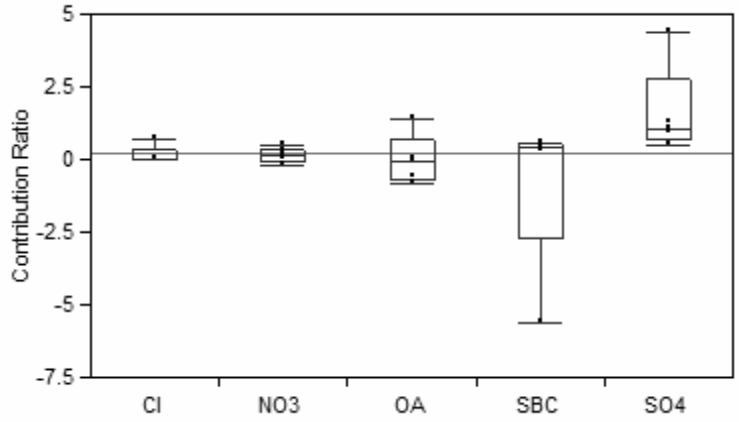

Figure 5. Box Plot of relative ion contribution ratios for M3 storms

Site M1 on the Middle Prong showed no discernable pattern for a common mechanism of acidification. Sulfate, nitrate, organic acids, and cation dilution were alternately responsible for the observed ANC depressions. Nitrate and sulfate contributions are responsible for three episodes, organic acids dominate two episodes, and one episode is controlled by cation dilution. With the exception of one storm, increases in cation concentration were significant to offset ANC decreases.

Site M2 on Ramsey Prong was consistently influenced by pulses of nitrate and sulfate. Nitrate contribution was the dominant mechanism for two storms occurring during the winter months. The steady ionic contribution from nitrate and sulfate indicate acid deposition may be an important acidifying mechanism in the Ramsey Prong watershed. Two events collected during the summer months were strongly influenced by increased organic acidity. Sum of base cation increases were a significant quantity to offset ANC decreases for each storm collected.

ANC changes at M3 on Eagle Rocks Prong were controlled primarily by increased concentrations of sulfate. Organic acids were insignificant with the exception of a storm on 10/27/06. Nitrate and sum of base cation changes were generally insignificant in overall changes to ANC. M3 was the only site that regularly experienced cation dilution, although not at a level to significantly change ANC.

The ion contribution data were analyzed for differences between sites, but only nitrate contribution between M2 vs. M3 was statistically different ($p= 0.014$) (Table 6). As the site differences for M1 vs. M2 vs. M3 were not significantly different, the data were pooled and analyzed for seasonal differences in ion contribution (Table 7). The

Table 6. Mann-Whitney U-test p-values for site differences in ANC contribution

Comparison	ΔCl/ΔANC	ΔNO3/ΔANC	ΔSO4/ΔANC	ΔSBC/ΔANC	ΔOA/ΔANC
M1 vs M2	0.454	0.088	0.670	1.000	0.394
M1 vs M3	0.068	0.584	0.273	0.361	0.068
M2 vs M3	0.086	.014*	0.221	0.142	0.624
M1 vs M2 vs M3	0.099	0.051	0.395	0.393	0.210

(* indicates the test is significant at $p<0.05$ level)

Table 7. Mann-Whitney U-test p-values for seasonal differences in ANC contribution

Season	ΔCl/ΔANC	ΔNO3/ΔANC	ΔSO4/ΔANC	ΔSBC/ΔANC	ΔOA/ΔANC
Dormant vs. Transpiring	0.860	0.906	0.239	0.126	0.195

contribution ratios were not statistically different for the pooled seasonal data. The p-values from the site and seasonal Mann-Whitney U-tests are available in Tables 6-7.

Effect of Watershed Hydrology on Stormflow Chemistry:

The storm data set was explored to find a possible relationship between the soil antecedent moisture condition, the maximum streamflow, and the magnitude of the pH change. The pH change was used to infer event magnitude rather than the ANC change due to the limited number of storms collected compared to the large quantity of sonde data available. The results of the 3-way data for each site are available in Figures 6-8. The figures indicate the largest pH depressions occur during high flow events preceded by dry weather.

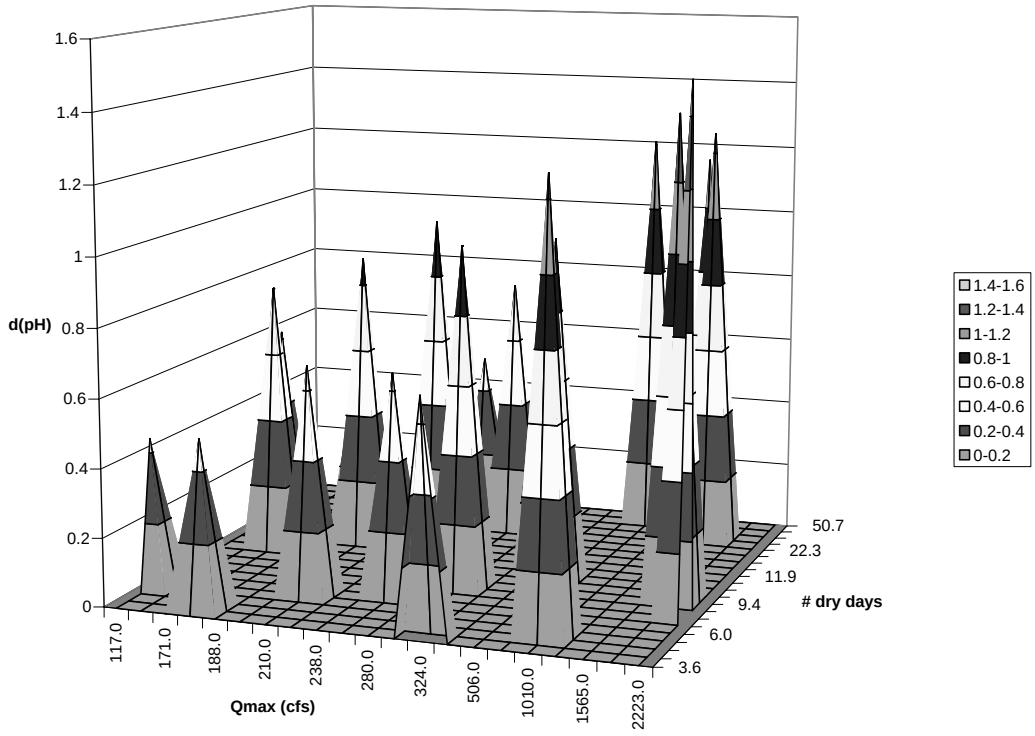

Figure 6. M1 pH response versus maximum flows and number of prior dry days

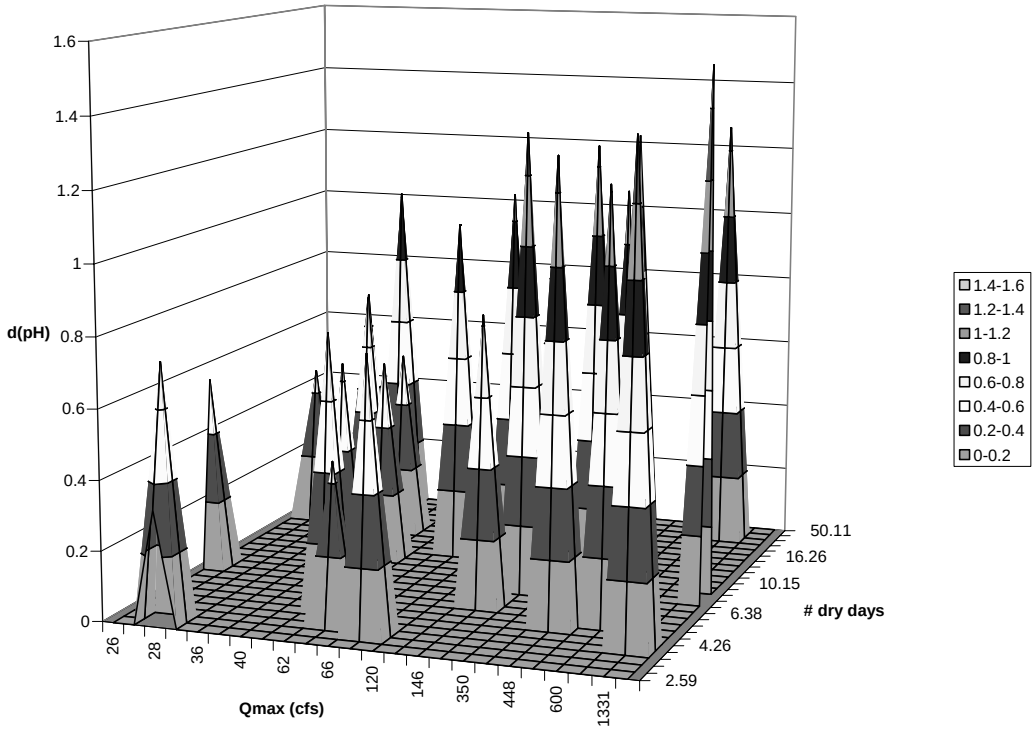

Figure 7. M2 pH response versus maximum flows and number of prior dry days

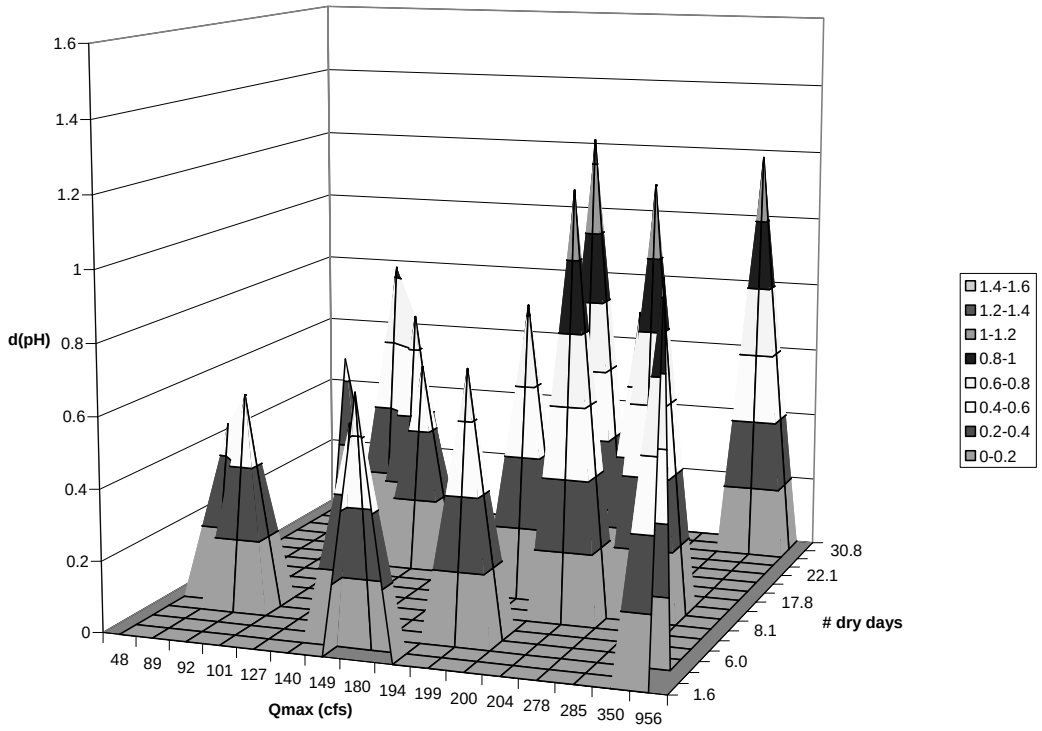

Figure 8. M3 pH response versus maximum flows and number of prior dry days

DISCUSSION:

The baseflow and stormflow stream chemistry differences were attributable to stormflow flushing the canopy and soil of sulfate, nitrate, organic acids, and exchangeable base cations. The measured baseflow constituent concentrations are similar to those observed in other high elevation stream studies in the GRSM (Silsbee and Larson 1982, Cook et al. 1994). Concentrations of most ions increase during stormflow, especially acidic anions, which contributed to ANC depression. The sum of baseflow and stormflow acid anion concentrations was variable between sites, with M3 having the highest concentrations. The higher concentrations of sulfate and nitrate at M3 caused it

to have a 12.1 and 27.6% higher baseflow anion total and 13.4 and 19.7% higher stormflow anion total than M1 and M2, respectively (Table 3). The anion differences are reflected in M3 having the lowest baseflow and stormflow ANC and pH. The stream (M3) with the lowest baseflow ANC was observed to have the lowest stormflow ANC (Table 2), which is consistent with prior regional study (Hyer et al. 1995).

Seasonal trends were observed for nitrate concentration, although differences in seasonal ANC contribution ratios were not statistically significant (Tables 4 and 7). Greater baseflow nitrate concentrations occurred during the winter; Cook et al. (1994) observed similar nitrate seasonality and attributed the increased winter export to lower vegetation uptake, greater deposition, and rates of organic decomposition and nitrification exceeding plant requirements. The increased nitrate concentrations during the dormant season have potential to contribute to stream acidification, as observed at M2 during two winter storms. Other seasonal baseflow trends were observed, but were not as important in affecting baseflow ANC (Table 4).

Nitrate and sulfate are significant contributors to acidification at each site, although the ANC contribution ratios vary in magnitude and relative strength between sites. Their consistent contribution to acidification across the MPLP agrees with the hypothesis of the watershed being susceptible to acid deposition. Other regional work has cited the significance of acid deposition as the controlling acidification mechanism in low alkalinity waters of the Southern Appalachian mountains (Herlihy et al. 1991, Deviney et al. 2006). Acid deposition appears to be the dominant mechanisms of acidification in the MPLP watershed.

Two of the four events collected at M2 were strongly influenced by increased organic acidity. Several baseflow and stormflow samples were analyzed for DOC concentration. All stream samples had low DOC concentration (1.5- 4.5 mg/L), but the stormflow samples had a higher concentration than baseflow samples. This indicates the potential for organic acids to have a greater effect on acidification, which is consistent with the ANC ion contribution analysis. The contribution of organic acids to episodic events is noteworthy as effects have been less documented in the Southern Appalachians. Cook et al. (1994) observed higher dissolved organic carbon (DOC) concentrations during storm events in high elevation streams in the GRSM. Their research suggests the organic acids flushed from the riparian zone could be responsible for pH depressions during certain storm events. Other regional studies have found organic acids to be significant to episodic acidification (Hyer et al. 1995). The substantial influence of organic acids in the Ramsey Prong watershed may suggest the need to further study the role of organic acidity during episodic events in the MPLP watershed.

Acidification at M3 on Eagle Rocks Prong was primarily controlled by increased concentrations of sulfate. The presence of Anakeesta geology in 11% of the watershed may explain the dominance of sulfate during episodic events. However, it is believed that undisturbed Anakeesta does not significantly contribute to stream acidification. Anakeesta exposures in the MPLP would be difficult to locate as they would likely be landslides in the inaccessible, higher elevations of the watershed. Nevertheless, throughfall precipitation analysis indicates that M3 actually receives slightly less sulfate deposition in comparison to M1 or M2; i.e. 652 kg/ha in comparison to 671 and 756 kg/ha, respectively. Still, deposition rates may be spatially variable and more throughfall

collection sites should be installed for future research. Discrepancies could occur due to uneven deposition rates over localized topography or may reflect an inadequate collection area. The deposition data potentially advocate geologic contribution to explain the differences in stream sulfate concentration at M3, but deposition should be better characterized.

The variability in natural and anthropogenic acidification mechanisms at M1, compared to M2 and M3, may reflect the relationship between increased drainage area and the potential for mechanism variability. At M1, three storms are controlled by mechanisms resulting from anthropogenic influences, i.e., acid deposition, and three are controlled by natural mechanisms, i.e., organic acids and cation dilution. The variability of the M1 acidification mechanisms may reflect unique processes occurring in sub-watersheds. Precipitation volumes and chemistry indicate spatial variability in rainfall and deposition amounts across the MPLP watershed. Sonde data indicate the potential for inconsistent streamflow response between sites even with similar precipitation amounts. One may infer that as the drainage area gets larger, it becomes increasingly difficult to predict consistent acidification mechanisms due to the unique mechanisms and hydrological responses of sub-watersheds.

Data exploration indicates the largest pH depressions are associated with large storms preceded by long dry periods. The pH response is similar for all study sites. A regional study in the Northeastern United States found comparable results as dry conditions were associated with a stronger acidification response (Lawrence 2002). These results are consistent with the idea of dry deposition accumulating in the canopy and soil during dry periods, and then being flushed out during hydrologic events.

Lawrence (2002) also indicated the potential for buildup of sulfate, nitrate, and acidity during dry periods due to the mineralization of organic matter. Streams may experience a severe response as the accrued acids are flushed into the stream.

CONCLUSIONS:

Episodic acidification was observed at each study site in the MPLP watershed. Average declines in ANC of 13, 22, and 18 μeq/L and pH of 0.89, 0.92, and 0.81 units were observed in M1, M2, and M3, respectively. Increases in acid anions at all sites during stormflow resulted in lower ANC. All sites received high deposition of sulfate and nitrate, and high concentrations were observed during baseflow and stormflow. Organic acid concentrations were low (approximately 11 μeq/L) at all sites during baseflow, but increased during storms events. Increases in cation sums were an important quantity to offset ANC decreases at M1 and M2, but not M3. This may reflect a lesser supply of exchangeable cations at the highest elevations.

The mechanisms of acidification were different at each study site. Episodic events at M2 were strongly influenced by pulses of nitrate and sulfate, but were also influenced by organic acids during summer storms. M3 ANC changes were consistently controlled by increased concentrations of sulfate. The relative sulfate concentrations and deposition data indicate episodic events at M3 may be influenced by Anakeesta pyritic geology. M1 has irregular patterns of acidification mechanisms, thus indicating the potential for mechanism variance as the drainage area increases. The consistent acidic contribution of sulfate and nitrate seem to indicate acid deposition as the dominant mechanism of acidification across the MPLP watershed. Acidification contribution by

organic acids and cation dilution were observed, but less so than sulfate and nitrate. This observation of acid deposition as the dominant acidification mechanism is significant in that it agrees with the original hypothesis of the MPLP watershed being susceptible to acid deposition.

The most severe episodes at each site occurred following large storms preceded by dry conditions. Long dry periods allow for greater amounts of deposition to accumulate, and then large hydrologic events are most successful at flushing out the accrued acids from the soil and canopy. This phenomenon suggests the effects of dry and cloudwater deposition are substantial in building up acidity in the MPLP watershed.

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APPENDICES

Appendix A: Review of Literature

This literature review was conducted by identifying previous work in the research area of episodic acidification. Pertinent literature was identified to study various natural and anthropogenic sources for short term acidification in surface waters in the eastern United States. Researchers have done extensive work to quantify the sources and mechanisms responsible for episodic acidification, as well as measuring the response of aquatic organisms.

Databases such as Compendex, Web of Science, GeoRef, and SciFinder Scholar were used to find relevant articles. The key words used were: episodic acidification, storm events, organic acids, water quality, water chemistry, pH, hydrology, headwater streams, Anakeesta, mass balance, Great Smoky Mountains, and Appalachian. Previous theses in the department proved very helpful in identifying pertinent literature. The University of Virginia has conducted similar regional work on episodic acidification in Shenandoah National Park.

Basic Hydrology:

The hydrologic behavior of the MPLP watershed may be approximated by comparison with the Coweeta Long Term Ecological Research (LTER) watershed in western North Carolina. Coweeta LTER has some of the longest continuous records of hydrological research in the southern United States. The Coweeta watershed has similar elevation, average temperature, soil type, soil depth, vegetation, and precipitation as the MPLP study area. The water budget of the Coweeta watershed was determined by analyzing historical hydrologic records. The average annual precipitation,

	Small Storm			Large Storm		
Antecedent Moisture Condition	Rainfall (mm)	Peak Flow (L/s/ha)	Storm Flow Volume (mm)	Rainfall (mm)	Peak Flow (L/s/ha)	Storm Flow Volume (mm)
Wet	30	1.1	21	157	6.8	49
Dry	59	1.5	5	102	3.3	9

Figure 9. Figure illustrating the effects of antecedent moisture, storm magnitude, and stream response

evapotransporation, and runoff are 173cm, 78cm, and 95cm, respectively (Sun et al. 2002). Sun, McNulty et al. (2002) quantified the Coweeta watershed response to storms of different magnitude and antecedent moisture condition. Wet or dry antecedent soil moisture conditions were determined by relative comparison to streamflow conditions. Peak flow rate and storm flow volume were the indicators used to identify the watershed's response to a storm event, detailed in the Figure 8. The data give evidence that the ratio of storm flow volume to rainfall is highly dependent on antecedent moisture conditions and the size of the storm event.

Potter, Lynch et al. (1988) performed a study in the Leading Ridge Experimental Watersheds (LREW) in central Pennsylvania. Their presentation of stormflow generation theory suggests four sources for streamflow: overland flow, deep groundwater flow, direct channel interception, and shallow subsurface stormflow. Direct runoff rarely occurs, even during large storms, because most forests have high infiltration rates. Potter and Lynch et al. cite previous research that finds storm event water may contribute less than 25% of streamflow during storm events. Many researchers believe that stormflow in headwater streams is due mainly to the displacement of pre-event soilwater. The rising water table increases the hydraulic gradient in the soil, thus causing drainage to areas of lower hydraulic head. The LREW study found that 97% of the total stormflow volume

from a summer storm event was transported to the river by subsurface sources. This indicates groundwater flow is the dominant transport mechanism for water reaching the channel.

The Great Smoky Mountains National Park (GRSM) receives an average precipitation of 141 cm. The Alum Cave Bluffs Parking Area station, which is more representative of the Middle Prong of the Little Pigeon River (MPLR) study site, receives an average of 200 cm precipitation. The climate is described as perhumid mesothermal with precipitation distributed throughout the year (Busing 2005).

Episodic Acidification:

Episodic acidification of surface waters can be described as the short term decrease in acid neutralizing capacity associated with precipitation or spring snowmelt. Episodic acidification is a ubiquitous process that has been observed in the eastern United States, Canada, and Europe (Hyer et al. 1995). The severity and duration of an episodic event may vary seasonally and regionally. Some studies find episodic acidification occurs more frequently in periods of high precipitation and less often during summer as transpiring vegetation absorbs soil moisture (Lawrence 2002). A study in Maine indicated episodes occur more frequently in the spring and fall, where the autumn episodes were shorter and more severe (Kahl et al. 1992). Short term acidification in streams can result from acid deposition, the mobilization of organic acids, the release of acid by pyritic geology oxidation, and the dilution of base cations associated with high stream flow (Tranter et al. 1994, Lawrence 2002).

A common measure of stream acidity is acid neutralizing capacity (ANC). ANC is essentially the ability of the stream water to neutralize an equivalence of strong acid, which can be determined by titration in a laboratory environment. Low ANC streams (<20 μeq/L) have little capacity to buffer acidic inputs to surface waters (Deviney et al. 2006). Streams that are susceptible to episodic acidification tend to share several features. Deviney, Rice et al. (2006) used regression equations and recurrence interval models to determine that streams collecting small catchments, high elevations, and less basaltic/carbonate rock will experience more severe ANC decreases. Baseflow ANC was found to be closely tied bedrock geology, in accordance with previous literature (Hyer et al. 1995).

Mechanisms of Episodic Acidification:

The associated chemistry of a given episode is subject to a great deal of variability. The episode chemistry is defined by the type of precipitation event, hydrologic flowpaths utilized, chemical reactions occurring in the soil, and antecedent moisture condition of the soil (Wigington et al. 1990, Tranter et al. 1994). Given the high degree of variability associated with each of the former quantities, one may infer that a watershed may have episodes of different magnitude, duration, and severity.

Baseflow stream water derives from groundwater flow in the lower part of the mineral soil. Water residing in the deeper soil has more time to interact with base cations. Stormflow is routed through the upper layers of the soil, which are generally more acidic due to acid deposition or natural processes. The storm water has less time to react with base cations in the soil and is generally more acidic upon delivery to surface

waters (Wigington et al. 1996b). Soil macropores may also play an important role in shallow groundwater flow because they allow acidic rain water to reach the stream quickly, thus minimizing the potential for acid buffering (Potter et al. 1988). As a result of these processes, baseflow water is more alkaline, i.e., higher ANC, than stormflow water.

The mechanisms of acidification are important in understanding why streams suffer from episodic acidification. Short term acidification processes in streams are associated with (1) increased concentrations of sulfate and nitrate from acid deposition, (2) the mobilization of organic acids, (3) increased acidity due to pyritic geology oxidation, and/or (4) the dilution of base cations caused by high stream flow (Tranter et al. 1994, Lawrence 2002). The chemical changes associated with episodic acidification are due to the complex interaction between these natural and anthropogenic factors. The first three acidifying factors depress ANC by acid-base chemistry reactions in groundwater and stream water. Additionally, increased stream flow during storm events causes a dilution of most solutes. The fourth acidifying mechanism is caused by the reduction of base cation concentration during high stream flow, thus causing a "dilution" effect in lowering ANC (Kahl et al. 1992).

ANC can be calculated as the total alkalinity of an unfiltered sample of water. ANC is dependent on the acid-base chemistry and total carbonate concentration of the water. ANC may be determined as:

$$ANC = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

For acidic waters, the concentrations of carbonate (CO3-) and hydroxide (OH-) are negligible. ANC can then be represented as:

$$ANC = [HCO_3^-] - [H^+]$$

ANC can also be equated by manipulation of the ion balance, where the concentration (μeq/L) of cations is equal to that of anions.

$$[Ca^{2+}] + [Mg^{2+}] + [K^+] + [Na^+] + [NH_4^+] + [H^+] =$$
$$[OH^-] + [HCO_3^-] + [CO_3^{2-}] + [NO_3^-] + [Cl^-] + [SO_4^{2-}]$$

By combining the above equations, we can determine ANC (μeq/L) from the ion balance as:

$$ANC = [HCO_3^-] - [H^+] = \sum [Cations] - [SO_4^{2-}] - [NO_3^-] - [Cl^-]$$

Few acidification events occur solely due to cation dilution; rather, base cation dilution in addition to increased acidic inputs causes episodic acidification. ANC losses are generally the result of a combination of the two processes, where acid-base reactions are more dominant than base cation dilution (Kahl et al. 1992). Therefore, episodic acidification may occur from any of these ANC diminishing processes, but often functions as a combination of multiple processes.

Stormflow enables stream acidification as acid deposition and/or naturally occurring acids are flushed from shallow soils in the watershed. The anions in stream flow (i.e., sulfate, nitrate, organic anions) are used to quantify acidity in the watershed. As such, the anions are not directly responsible for acidification, but reflect the presence of acids in the soil. Wellington and Driscoll (2004) estimated the change of concentration for specific ions and their respective contribution to an ANC change during storm events. The ionic contributions were determined as follows:

$$dC_B = (C_{Bp} - C_{Be}) / \Delta ANC$$
$$dSO_4^{2-} = (SO_{4e}^{2-} - SO_{4p}^{2-}) / \Delta ANC$$
$$dNO_3^- = (NO_{3e}^- - NO_{3p}^-) / \Delta ANC$$
$$dCl^- = (Cl_e^- - Cl_p^-) / \Delta ANC$$
$$dA^- = (A_e^- - A_p^-) / \Delta ANC$$
$$\Delta ANC = ANC_p - ANC_e$$

Where the subscripts "p" and "e" represent the pre-event and ANC minimum values, respectively. ΔA^- indicates the change in organic anion concentration. Positive ratio values indicate contribution to ANC depression, while negative values indicate ANC increase.

Many regional studies have been conducted to determine the dominant mechanisms of episodic acidification. Many episodes in the Northeast, especially in the Adirondack and Catskill Mountains, are associated with strong nitrate pulses (Wigington et al. 1990). Pulses of sulfate are observed with ANC depressions in Pennsylvania and mid-Atlantic states (Herlihy et al. 1991). Sea-salt effects dominate the episodes in the coastal areas of Maine (Kahl et al. 1992). Organic acidity is a major acidifying mechanism in low-gradient streams with elevated concentrations of dissolved organic carbon (Herlihy et al. 1991, Wellington and Driscoll 2004).

Acid Deposition:

Atmospheric acid deposition can have deleterious effects on stream water quality and aquatic biota. Acid deposition may be described as the sum of wet (precipitation), dry (gases and particles), and cloud water deposition (Lovett and Kinsman 1990, Roby 2005). Acid deposition has been monitored for several decades and is predominantly the

result of anthropogenic pollutants. Sulfur and nitrogen compounds are released into the atmosphere where they react to form sulfuric and nitric acids. The primary source of sulfur emissions in the eastern United States is from coal-fire power plants, while the dominant source of nitric oxide emissions are from the combustion of petroleum products in vehicles (Baird and Cann 2005).

The effects of acid deposition may be realized in a watershed in several ways. Acid deposition may cause decreased ANC in stream flow, thus a resulting pH depression. The lower pH has the potential to change the chemical speciation in stream water, particularly noteworthy is the solubility of aluminum, which may prove toxic to trout at pH < 5 (Baird and Cann 2005, Roby 2005) . Long-term atmospheric deposition may result in conditioning the watershed by accumulation of sulfate, nitrate, ammonium, and proton (Wigington et al. 1996a) The leaching of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) is another negative effect of acid deposition. The loss of base cations robs vegetation of essential nutrients, as well as increasing the potential for leaching aluminum out of the soil (Roby 2005).

Trends for atmospheric deposition have been measured temporally and spatially in the GRSM. The EPA has a monitoring station at Elkmont (elev. 2100-ft) as part of the National Atmospheric Deposition Program (NADP), which has been monitoring wet deposition since 1980. The University of Tennessee has maintained a monitoring station at the Noland Divide Watershed (NDW) (elev. 5900-ft) since 1991 to monitor stream water quality and atmospheric deposition. The NADP historical data at Elkmont shows that while the concentration of acidic wet deposition is decreasing, the annual mass deposited is remaining fairly stable due to the trend of increased precipitation (National

Atmospheric Deposition Program (NRSP-3)). The annual flux of nitrate, ammonium, and chloride appear to be remaining stable, while the mass deposition of sulfate has decreased, presumably due to tighter emissions controls for coal-fire power plants. The NDW results show increasing depositions of nitrate, ammonium, and chloride, while the sulfate deposition is decreasing.

Several excellent sources of literature were located to identify the potential for spatial variation and distribution of atmospheric deposition (Lovett and Kinsman 1990, Baumgardner et al. 2003). Two factors can be considered to quantify wet deposition: the quality and quantity of precipitation at a given elevation. Wet deposition of sulfate, nitrate, and proton has been shown to increase at higher elevations because of higher rainfall associated with orographic precipitation. Cloud water deposition can be quite significant for high elevation sites, but may vary significantly due to wind speed, cloud structure, and canopy type. The resulting deposition is inherently uneven as these factors are variable and weather patterns are spatially unique.

Organic Materials Influencing Stream Acidification:

Stream acidification may occur as organic acids are flushed from the soil horizon during storm events. The influence of organic materials can be quantified by measuring the dissolved organic carbon (DOC) concentration in stream flow (Herlihy et al. 1991). Waters with high concentrations of DOC can be acidic due to their organic acid content, where humic substances may comprise approximately 50 percent. Humic substances, whose composition are poorly understood, are complex substances comprised of humic acids, fulvic acids, and humin (Eaton et al. 2005). Streams with DOC concentrations of

1-10 mg/L can be considered "organic influenced." Streams with organic anion concentrations greater than the sum of sulfate and nitrate concentrations would be considered "organic dominated" (Herlihy et al. 1991). Wellington and Driscoll (2004) utilized a method of estimating organic anion concentration [A-] by calculating the difference in the water's charge balance.

$$[A^-] = \sum C_c - \sum C_a - ANC$$

where: $$\sum C_c = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+] + n[Al^{n+}]$$

and: $$\sum C_a = 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] + [F^-]$$

The charge of aluminum can be determined by using speciation calculations and chemical equilibria (Wellington and Driscoll 2004). This approach assumes that any difference in charge balance is due to organic anions and not analytical error. Strong and weak organic anions can be estimated by:

$$[A_S] = \sum C_c - \sum C_a - ANC_G$$

$$[A_W] = [A^-] - [A_S]$$

Where ANC_G is the experimentally measured Gran ANC (http://pubs.water.usgs.gov/twri9A6 /).

The anion compositions of streams in the National Stream Survey were evaluated to determine the causes of acidity in low ANC streams (Herlihy et al. 1991). Their regional study determined that streams in the Southeastern highlands were not dominated by organic acidity, but did not eliminate the contribution of organic acidity. For streams in the Southeastern highlands, the study determined that "the vast majority were classified as inorganic," where the acidity was primarily due to acid deposition.

Further studies have indicated that organic acidity may play a significant role in episodic acidification (Herlihy et al. 1993, Cook et al. 1994) One such study conducted in Hubbard Brook Experimental Forest in New Hampshire determined that the flushing of organic acids was a dominant contributor to acidification during rainfall events. This phenomenon was exacerbated by wet antecedent moisture conditions. Conversely, the influence of organic acids was only a minor contributor during snow melt (Wellington and Driscoll 2004).

A separate study in the Great Smoky Mountains found that DOC levels increased by 200 μmol/L in one spring storm, thus contributing to a pH drop of one unit, possibly due to an increase in organic acids (Cook et al. 1994). Baseflow DOC concentrations were considerably lower that those observed in stormflow. Organic acidity increases of 220-320 μmol/L were observed during storm events. This increase is most likely attributable to the separate flowpaths stormflow and baseflow utilize to reach the stream. Stormflow routed through shallow soil could transport organic acids from the organic-soil horizons. Baseflow derives from the lower mineral soil that tends to sorb DOC (Cook, Elwood et al. 1994). Multiple linear regressions indicate changes base cation concentrations and nitrate were the most significant quantities for stream acidification in this study. Generally, changes in DOC concentration did not have statistically significant trends for affecting ANC depressions.

Geologic Factors Influencing Stream Acidification:

Pyritic geology is a potentially significant source of acidification for surface waters. Anakeesta formations are a type of pyrtic rock commonly found in high

elevations of the Great Smoky Mountains. Anakeesta is comprised of carbonaceous and sulfidic slate or mica schist, as well as varying quantities of sulfide (Bacon and Maas 1979). Anakeesta is relatively non-reactive until exposed to air and water, whereupon it oxidizes to releases acid and heavy metals (i.e., zinc, manganese, aluminum, and copper) to adjacent bodies of water. Sulfate is generally the highest concentrated anion in streams contaminated by Anakeesta oxidation (Minear and Tschantz 1976). Numerous studies have cited the damaging effects resulting from Anakeesta leachates impacting aquatic organisms (Huckabee et al. 1975, Bacon and Maas 1979, Kucken et al. 1994). As a result of past studies, efforts have been made to avoid construction practices that expose Anakeesta formations, especially in road construction within the GRSM.

Stormflow vs. Baseflow Water Quality:

Stormflow and baseflow water quality is important in understanding the dynamics of chronic and acute acidification in surface waters. There are gaps in the understanding of processes controlling episodic acidification of surface water and the severity of the problem (Herlihy et al. 1993, Hyer et al. 1995). Hyer, Webb et al. (1995) cite that the episodic acidification data is especially incomplete in the southeastern United States, thus more research is required.

Hyer, Webb et al. (1995) conducted a study in Shenandoah National Park (SNP), Virginia, to evaluate the changes in acid-base chemistry during storm events, the hydrologic paths controlling ANC, and the contribution of specific ions to ANC depression during storm events. Three watersheds were selected based on similar stream discharge, catchment areas, and acidic deposition rates. However, each of the three

watersheds had differing bedrock geology, baseflow ANC, and baseflow pH. The sites were monitored for 3 years and water quality was analyzed for pH, ANC, dominant cations, dominant anions, and aluminum. Twenty-five separate storms occurred and nearly all of the episodes occurred while the streams were at baseflow conditions, thus allowing comparison of baseflow vs. stormflow water quality. Each storm event had a corresponding stream flow depression of ANC and increase of acidic anions (i.e., sulfate, nitrate, and organic anions) regardless of antecedent moisture conditions, which was consistent with previous studies in SNP (Obrien et al. 1993).

Their findings, represented below in Figure 9, indicate that increased concentrations of acidic anions and the dilution of base cations were the most important mechanisms in stream acidification. The relative contribution of each anion was calculated from the difference of baseflow and ANC_{min} concentrations divided by the total ANC change, as discussed previously in Mechanisms of Episodic Acidification. Hyer, Webb et al.'s findings indicate that episodic acidification is occurring in each watershed, despite unique geologies and varying acidification mechanisms. Streams with the lowest baseflow ANC experienced the least change in ANC during storm events, though they reached the lowest minimum ANC values and were most susceptible to episodic acidification. This study allows for prediction of sensitivity to episodic acidification, assuming the three sites' geologies are representative of the entire SNP. Episodic acidification can be considered a ubiquitous process in SNP and watershed sensitivity may be inferred from bedrock geology.

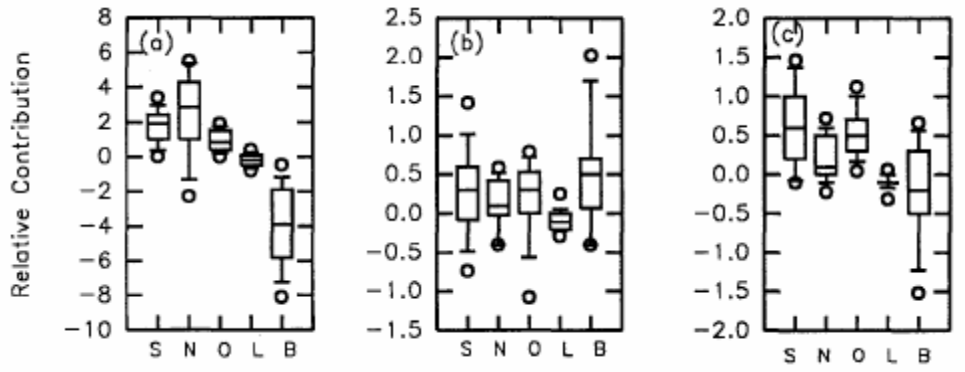

Figure 10. Box plots of relative contribution of each ion to ANC loss observed in (a) Paine Run, (b) Piney River, and (c) Staunton River. S is sulfate, N is nitrate, O represents strong organic acids, L is chloride, B is sum of base cations (Ca, Mg, Na, K). Positive values indicate ANC loss. The horizontal line in each box is the median value, other lines indicate the 10th, 25th, 75th, and 90th percentiles. (Source: Hyer, Webb, et al. (1995))

Impacts of Episodic Acidification on Trout and Macroinvertabrates:

Brook trout are unique in that they are the only native trout found in the GRSM. Brook trout were once found throughout the Park, but now are only present at elevations above 3500-ft (Roby 2005). The National Park Service is concerned about the impacts of acidification and the survival of brook trout. Many researchers have noted that elevated concentrations of metals in acidified streams prove toxic to fish (Potter et al. 1988). Barnett presents extensive information regarding the effects of pH and resulting metals concentrations on trout health. The response of trout may include avoidance of particular areas, reduced size, and mortality of adults and eggs. Trout exposed to chronic acidification exhibit a more sensitive response to acidic episodes, as is often the case in high elevation streams in the GRSM (Roby 2005). Other factors affecting the survival of brook trout are loss of habitat, migration barriers, and competition with non-native fish (Hansen et al. 2002).

Potter, Lynch et al (1988) discuss the negative effects of acidification on various aquatic organisms in freshwater systems. They note that chronic and acute acidification have damaging effects in that insect fauna suffer mortality in low pH streams in the Laurel Hills of Pennsylvania. Further literature is available to explore the comprehensive effects of acidic streams and the health of aquatic organisms (Haines 1981).

Appendix B: Mass Balance Analysis

Methods:

A mass balance was performed in effort to understand watershed behavior and quantify the responsible mechanisms for episodic acidification, i.e. acid deposition, organic acid mobilization, pyritic geology, or cation dilution. An estimation of a watershed mass balance was made by quantifying the chemical solutes entering and exiting a watershed. The watershed response to a given storm varies dependent on rainfall volume, intensity, duration, and the antecedent moisture conditions of the soil. As such, the mass flux of ions associated with a single event will be variable as hydrologic conditions are unique for each storm and watershed. An annual mass balance was determined to be more practical to evaluate the net ionic flux because of the unique watershed response for individual events.

The deposition for each watershed was estimated from the throughfall precipitation concentration and volume. The rainfall volume was determined using bulk precipitation collectors. The product of the ionic concentrations and rainfall volume yields the mass of ions deposited in the watershed.

The ionic export from a watershed was determined by multiplying the streamflow volume by the solute concentration. Flow measurements at each site were determined from rating curves. Stage-to-discharge measurements were made at an established datum in accordance with USGS Water-Supply Paper 2175. Velocity measurements were made following the Six-Tenths Depth Method, where the average downstream velocity is be assumed to be 0.6 feet below the water surface (WSP 2175). Flow measurements were made at incremental distances to ensure no more than 10% of the streamflow occurred at

any cross-section. Flow measurements were taken at range of river stages to develop a rating curve, which was correlated with sonde stage measurements.

The goal of the annual mass balance is to evaluate responsible mechanisms for episodic acidification. Ionic exports were estimated for stormflow and baseflow to determine how mass is transported. During storms, ion concentrations were measured for each stormflow sample collected. The total ionic mass transported during the storm was determined from the chemistry and flow data associated with each storm sample. However, not every storm was collected due to equipment malfunctioning or power supply problems. Average ion concentrations were determined seasonally for each collected storm based on total ionic mass and stormflow volume. Average seasonal storm chemistry was applied to un-collected storms to estimate the mass moved during every event for the year. Similarly, ionic exports for baseflow were determined by the same procedure using streamflow volume and sample chemistry. Baseflow samples were collected monthly and/or before storms, and then analyzed to provide average seasonal chemistry data for each site. Seasonal chemistry and streamflow data were utilized to determine baseflow exports.

Results:

The mass balance was separated into an annual balance and a stormflow versus baseflow balance. The annual mass balance results are contained in Tables 7-9 and Figures 10-18 for M1, M2, and M3. The results for each site indicate a greater export than import for all quantities, except potassium and ammonia. Ammonia is presumably oxidized quite rapidly to nitrate once deposited into the watershed. Also, the proton

Table 8. Ionic flux comparison for annual deposition and stream export for M1

Quantity	Cl eq/ha	NO3-N eq/ha	SO4 eq/ha	NH4-N eq/ha	H ion eq/ha	ICP Na eq/ha	ICP K eq/ha	ICP Mg eq/ha	ICP Ca, eq/ha
Throughfall	156.7	179.2	670.5	211.9	193.0	166.2	578.2	274.1	564.8
Stream	236.2	638.7	984.5	15.6	135.7	533.4	209.7	548.9	1150.7

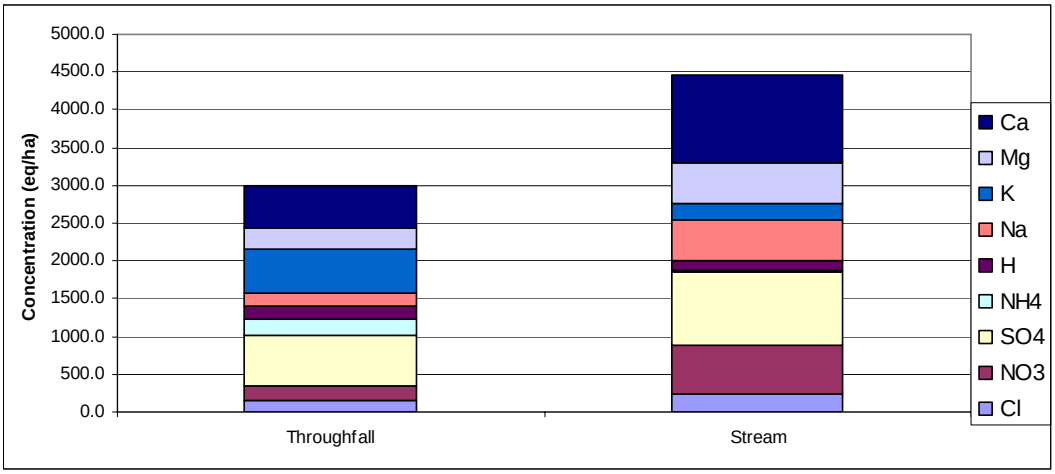

Figure 11. Comparison of annual ionic flux for site M1

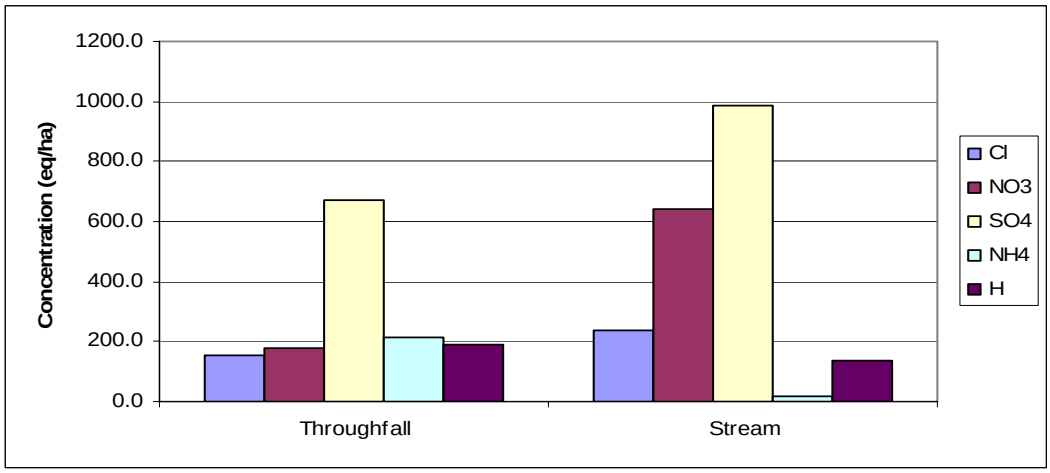

Figure 12. Annual anion and acid cation flux for M1

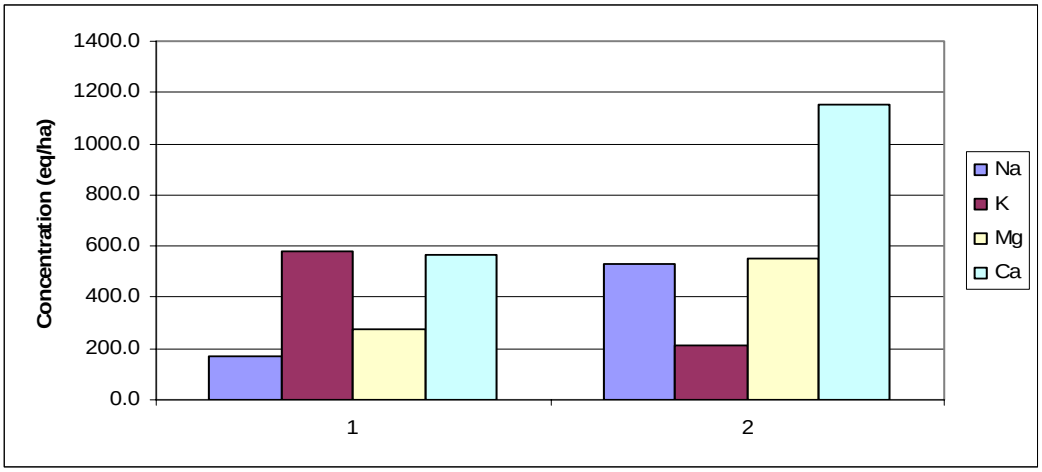

Figure 13. Annual base cation flux for M1

Table 9. Ionic flux comparison for annual deposition and stream export for M2

Quantity	Cl eq/ha	NO3-N eq/ha	SO4 eq/ha	NH4-N eq/ha	H ion eq/ha	ICP Na eq/ha	ICP K eq/ha	ICP Mg eq/ha	ICP Ca, eq/ha
Throughfall	192.6	136.4	756.2	136.2	107.1	159.7	778.0	295.5	590.4
Stream	188.6	583.5	760.8	11.6	146.7	438.8	222.5	369.5	890.1

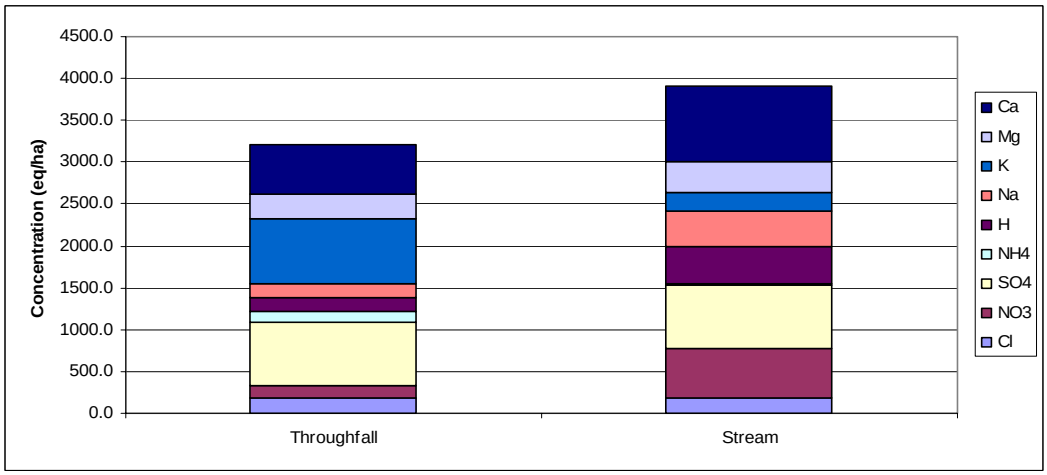

Figure 14. Comparison of annual ionic flux for site M2

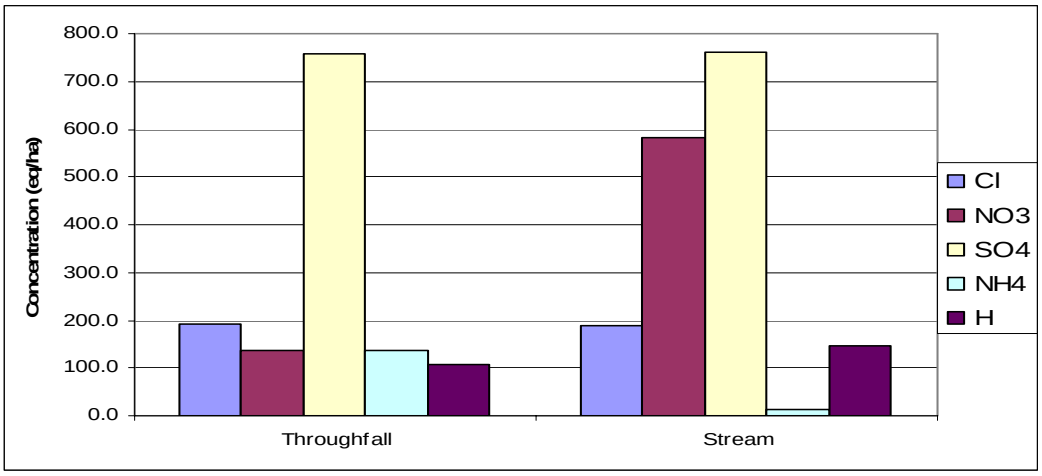

Figure 15. Annual anion and acid cation flux for M2

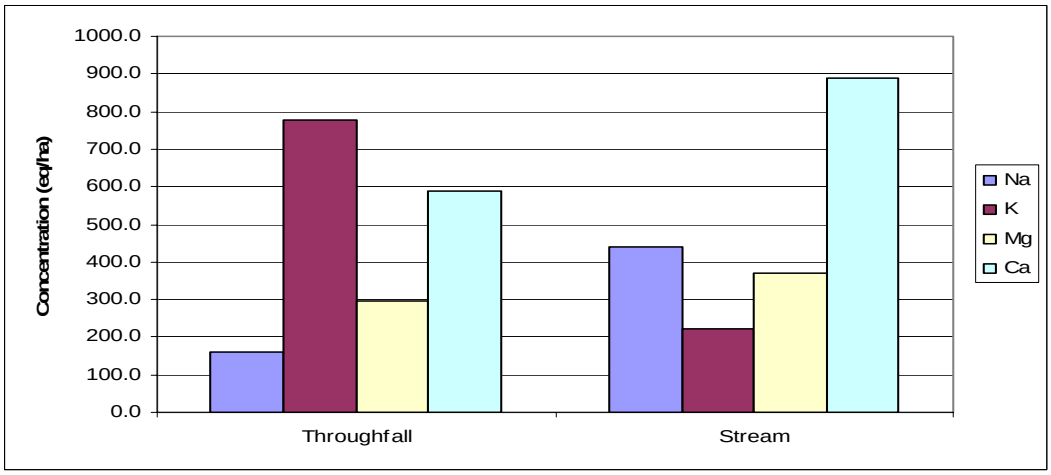

Figure 16. Annual base cation flux for M2

Table 10. Ionic flux comparison for annual deposition and stream export for M3

Quantity	Cl eq/ha	NO3-N eq/ha	SO4 eq/ha	NH4-N eq/ha	H ion eq/ha	ICP Na eq/ha	ICP K eq/ha	ICP Mg eq/ha	ICP Ca, eq/ha
Throughfall	163.4	230.6	651.8	282.8	361.6	232.0	439.1	281.8	517.8
Stream	318.1	1125.7	1545.8	16.5	362.0	631.4	228.1	887.2	1494.3

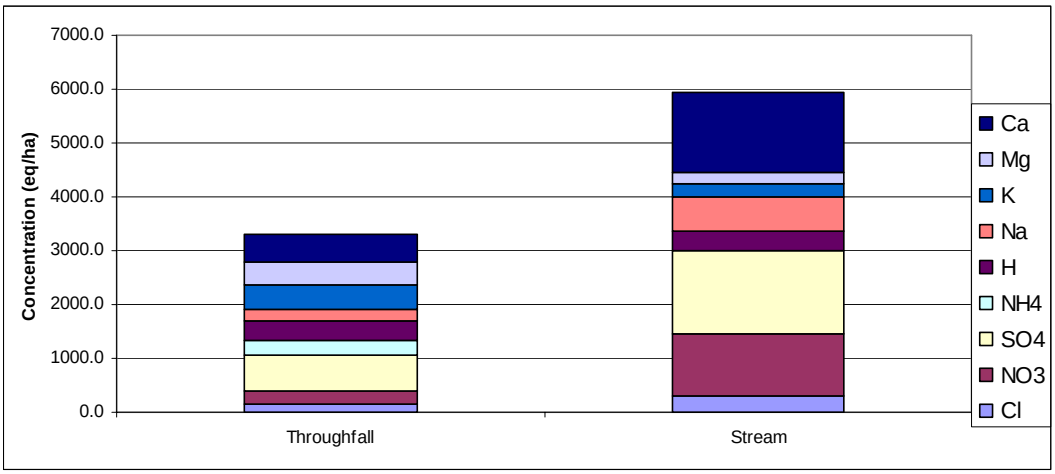

Figure 17. Comparison of annual ionic flux for site M3

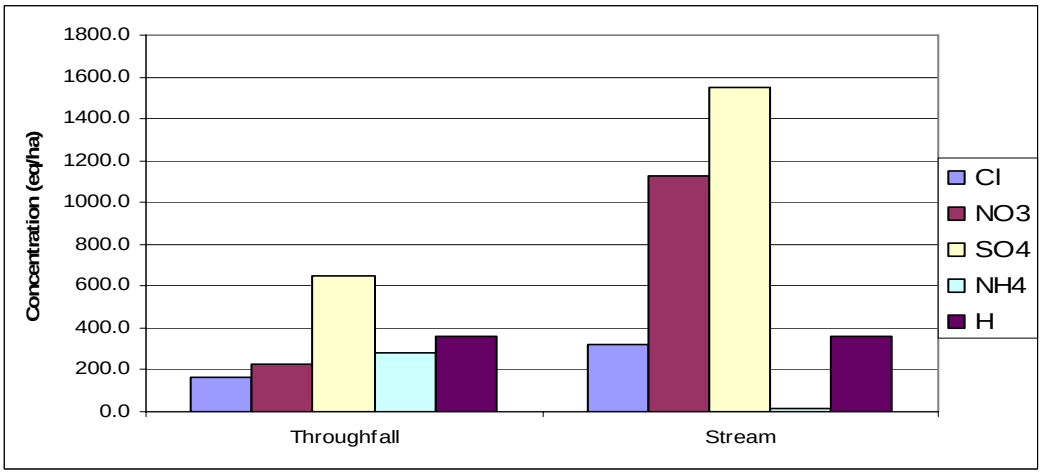

Figure 18. Annual anion and acid cation flux for M3

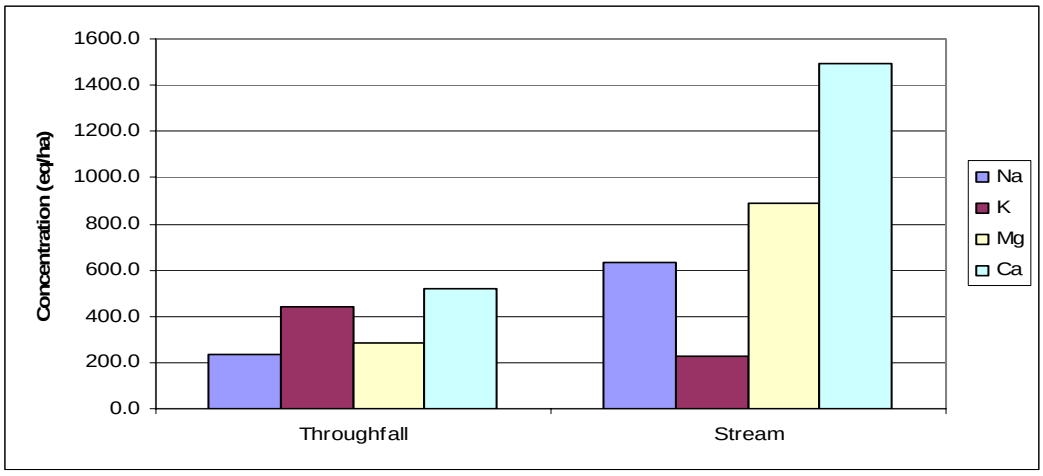

Figure 19. Annual base cation flux at M3

(hydrogen) budget shows some variability between sites. Site M3 is observed to have to have the highest exports of sulfate and nitrate.

The stormflow versus baseflow mass balance was also computed for each site (Tables 10-12 , Figures 19-27). The baseflow and stormflow total masses moved were different for each site: baseflow moved more than stormflow for M1, stormflow more than baseflow for M2, and baseflow and stormflow were nearly equivalent for M3. The individual ion masses are quite variable between sites, which is more reflective of the calculated volume of water transported than the chemical differences.

Table 11. Baseflow versus stormflow ionic flux comparison for M1

Quantity	Cl eq/ha	NO3-N eq/ha	SO4 eq/ha	NH4-N eq/ha	H ion eq/ha	ICP Na eq/ha	ICP K eq/ha	ICP Mg eq/ha	ICP Ca, eq/ha
Throughfall	156.7	179.2	670.5	211.9	193.0	166.2	578.2	274.1	564.8
Baseflow	163.0	356.9	635.3	5.6	88.1	385.3	130.6	362.3	769.4
StormFlow	73.2	281.8	349.1	10.0	47.7	148.0	79.1	186.5	381.3

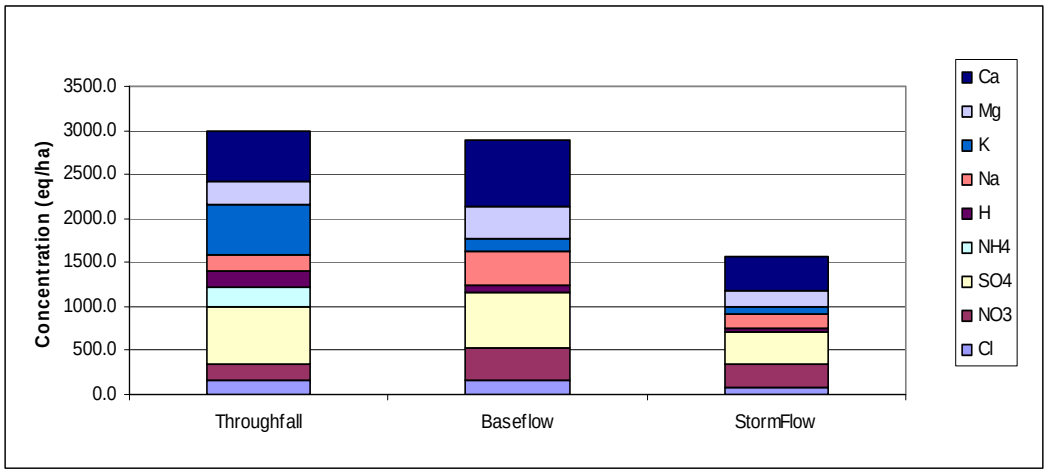

Figure 20. Comparison of baseflow and stormflow total ionic flux for M1

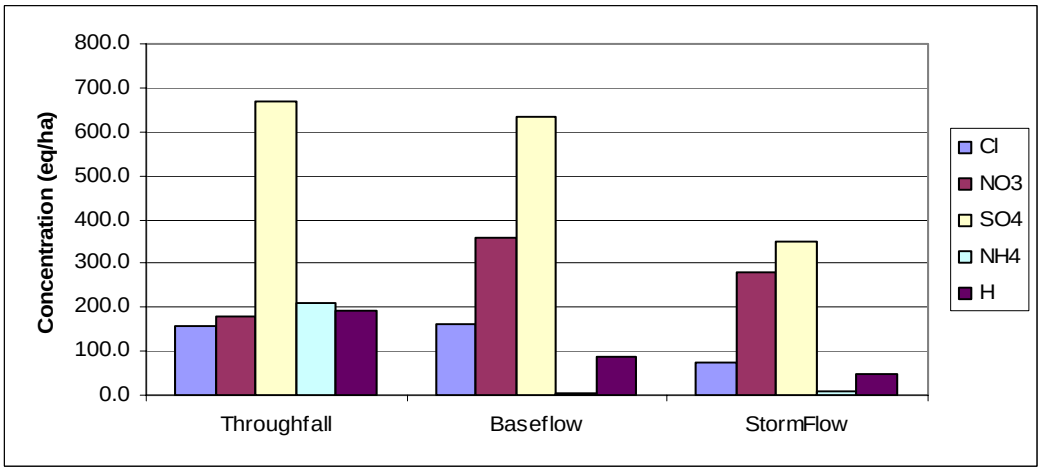

Figure 21. Baseflow versus stormflow anion and acid cation flux for M1

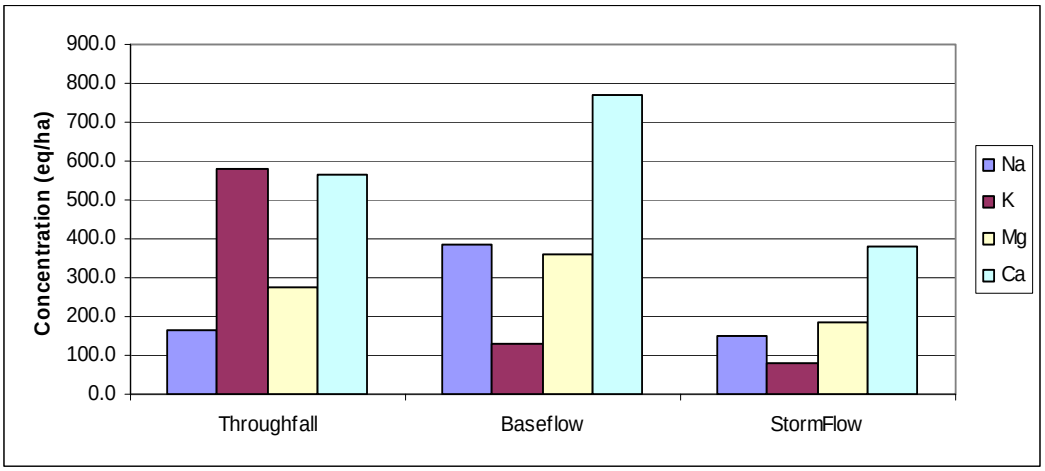

Figure 22. Baseflow versus stormflow base cation flux for M1

Table 12. Baseflow versus stormflow ionic flux comparison for M2

Quantity	Cl eq/ha	NO3-N eq/ha	SO4 eq/ha	NH4-N eq/ha	H ion eq/ha	ICP Na eq/ha	ICP K eq/ha	ICP Mg eq/ha	ICP Ca, eq/ha
Throughfall	192.6	136.4	756.2	136.2	107.1	159.7	778.0	295.5	590.4
Baseflow	89.8	153.9	303.6	2.9	48.5	207.4	88.2	141.4	337.5
StormFlow	98.8	429.6	457.1	8.8	98.2	231.4	134.3	228.1	552.6

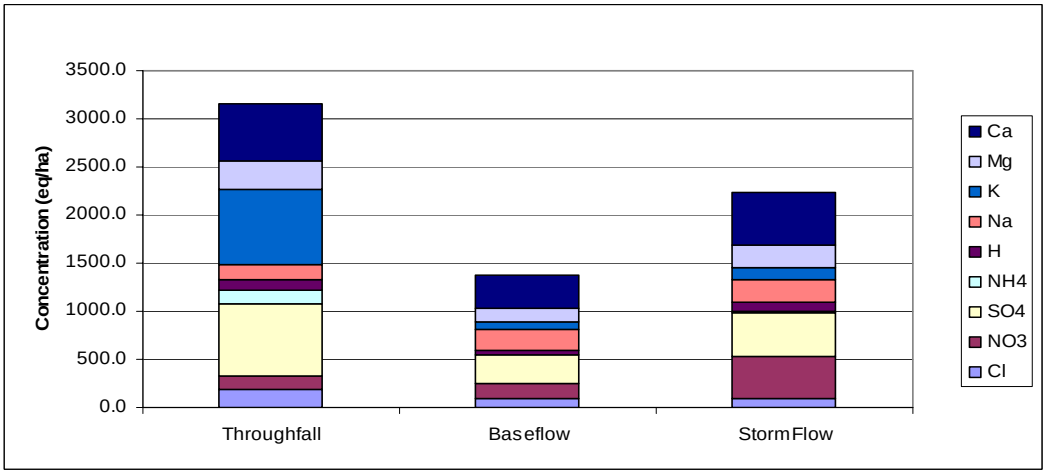

Figure 23. Comparison of baseflow and stormflow total ionic flux for M2

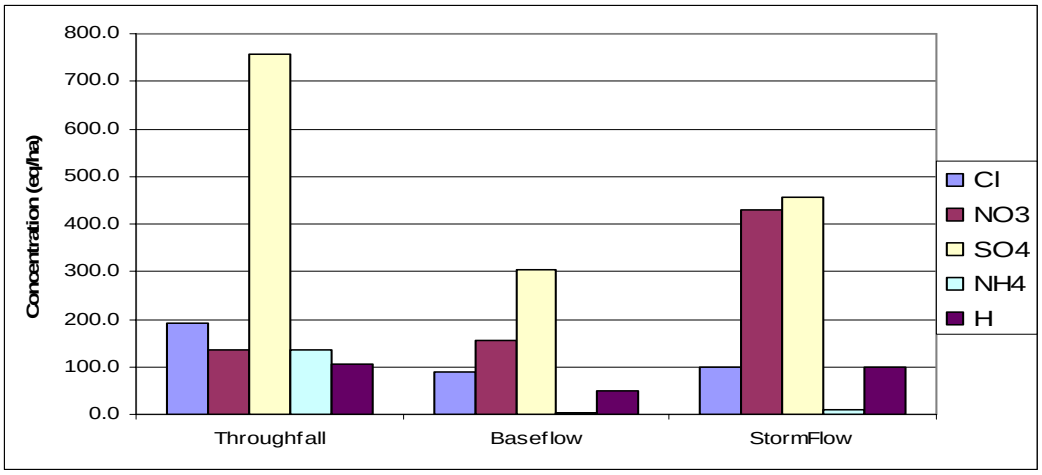

Figure 24. Baseflow versus stormflow anion and acid cation flux for M2

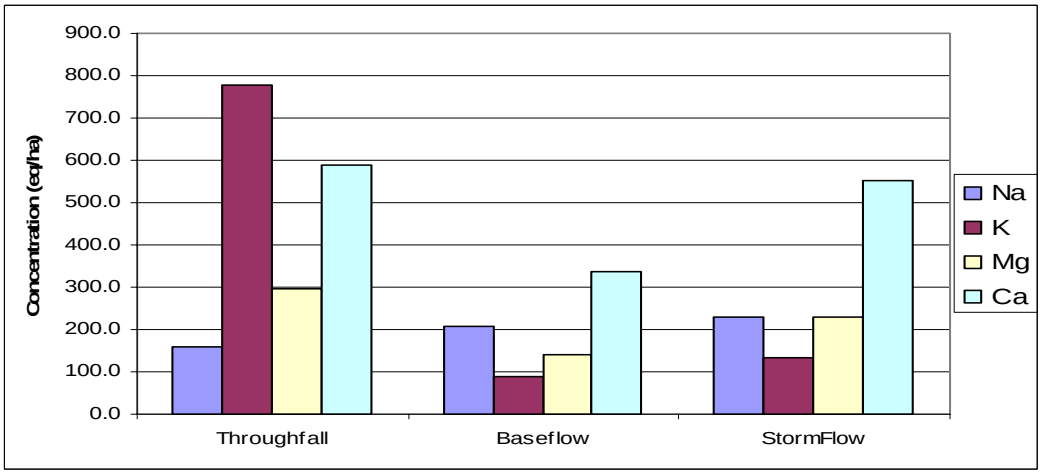

Figure 25. Baseflow versus stormflow base cation flux for M2

Table 13 Baseflow versus stormflow ionic flux comparison for M3

Quantity	Cl eq/ha	NO3-N eq/ha	SO4 eq/ha	NH4-N eq/ha	H ion eq/ha	ICP Na eq/ha	ICP K eq/ha	ICP Mg eq/ha	ICP Ca, eq/ha
Throughfall	163.4	230.6	651.8	282.8	361.6	232.0	439.1	281.8	517.8
Baseflow	177.4	450.7	761.8	6.3	128.9	413.1	131.4	479.5	834.0
StormFlow	140.6	675.0	784.0	10.2	233.1	218.3	96.7	407.8	660.2

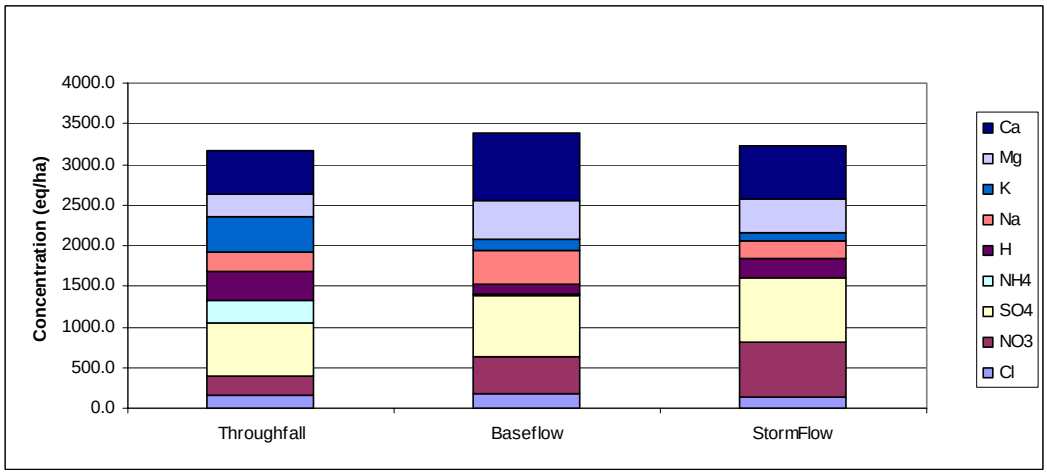

Figure 26. Comparison of baseflow and stormflow total ionic flux for M3

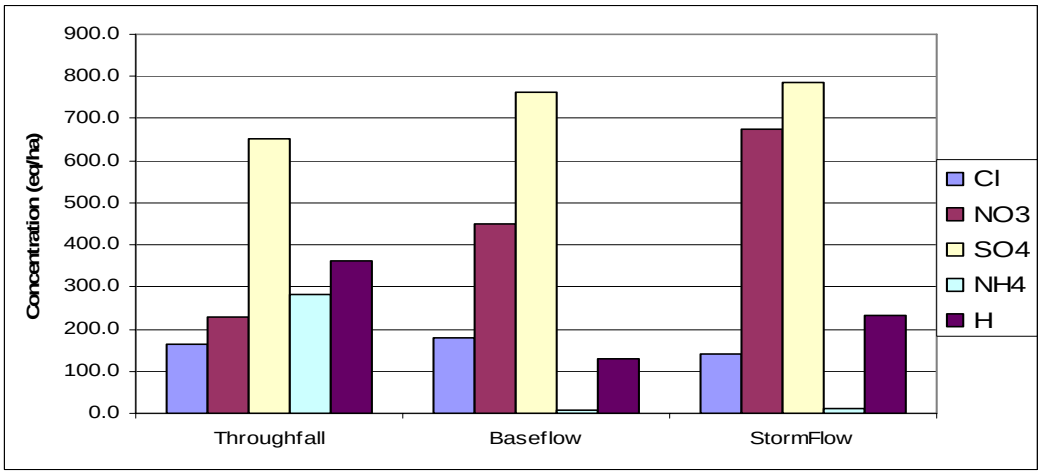

Figure 27. Baseflow versus stormflow anion and acid cation flux for M3

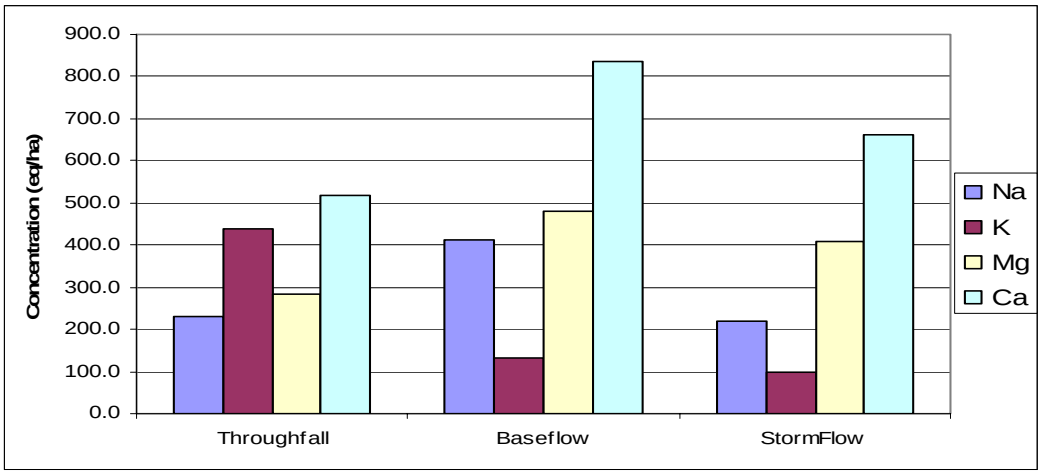

Figure 28. Baseflow versus stormflow base cation flux for M3

Discussion:

Conducting a mass balance at each site in the MPLP watershed was one of the primary objectives of the study. The goal was understand the ionic flux, and then apply the findings to develop a conceptual pollutant fate and transport model. The hopes were to identify acid sinks and sources and to better understand acidification processes. The researchers also hoped to better understand the respective ionic masses moved by baseflow and stormflow.

The rating curves proved to be the weakest link in the mass balance analysis. Insufficient rating curves made flow predictions unreliable. The most obvious bad flow data were the stormflow values. Peak flow values at M2 and M3 were post-modified to fall within a certain percentage of flow observed at M1. Flow values at M1 were compared to the downstream USGS gage in Sevierville. Additionally, there were gaps in

the sonde data that required estimation of depths. Depth estimations were estimated by inferring relative depths at the upstream or downstream site. There was inherent uncertainty in the mass balance due to the insufficient rating curves and data gaps. The net ionic fluxes and comparison of baseflow and stormflow mass movements were deemed to be misleading and erroneous.

The precipitation estimate for the MPLP watershed was approximately 200 cm/yr. The flow volumes yielded from the Middle Prong, Ramsey Prong, and Eagle Rocks Prong were 172, 153, and 239 cm/yr, respectively. These yields are clearly too high; Coweeta watershed data indicate yield should be approximately 55% of the annual precipitation. Summation of baseflow and stormflow volumes indicates both are too high, thus making further corrections difficult and probably unreliable.

The researchers ultimately decided to exclude the mass balance from the published manuscript due to analytical errors. Suggestions for improving this process might include utilizing a rating curve that better represents the full range of flow values. However, high flows would be difficult to measure as stormflow is dangerous in high gradient mountains streams. Another approach could be to utilize a hydrologic model that can predict flow values based on precipitation inputs and watershed characteristics. This method could also prove problematic due to the high variability in local precipitation and difficulty in representing watershed conditions. One must recognize the degree of difficulty in collecting real data in extremely remote environments.

Appendix C: Comparison of Throughfall Precipitation, Baseflow, and Stormflow Chemical Concentrations

A comparison of precipitation, baseflow, and stormflow concentrations was done in tabular and graphical form (Tables 14-16, Figures 29-34). The concentration data is unique from the mass balance data in that mass or equivalent mass per area was not considered, only chemical concentrations. Graphical results were organized to show the respective anion and cation concentrations in separate graphs. Acid anion concentrations were higher than precipitation concentration during baseflow and stormflow for M1 and M3, but not always for M2. Higher anion concentrations in streamflow may reflect additional sources of acid anions in the watershed, possibly from the mineralization of organic matter. More study is required to understand biogeochemical processes in these high elevation watersheds.

Table 14. Constituent concentrations for throughfall precipitation, baseflow and stormflow at M1

Quantity	Cl ueq/L	NO3-N ueq/L	SO4 ueq/L	NH4-N ueq/L	H ion conc, ueq/L	ICP Na ueq/L	ICP K ueq/L	ICP Mg ueq/L	ICP Ca, ueq/L
TF	12.5	14.4	41.9	12.3	16.1	11.8	31.1	17.2	42.5
Baseflow	11.0	36.3	45.2	0.2	2.9	27.6	11.1	24.1	50.8
Stormflow	11.0	38.1	53.9	2.0	4.6	23.8	12.7	29.7	56.7

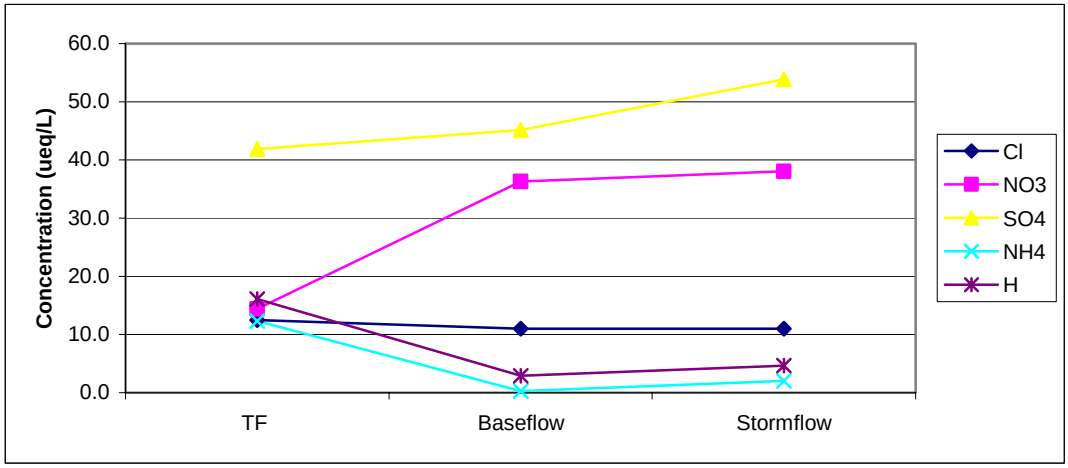

Figure 29. Anion and acid cation concentrations for throughfall precipitation, baseflow, and stormflow at M1

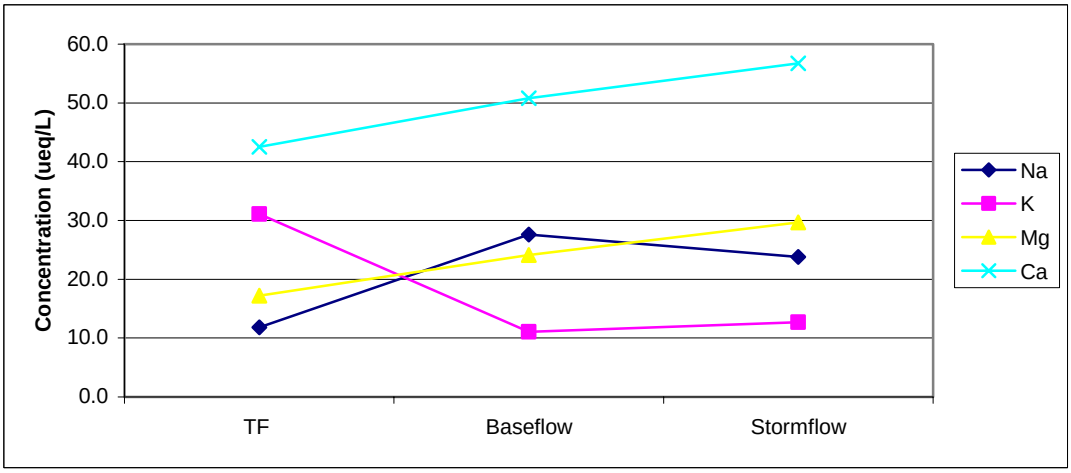

Figure 30. Base cation concentrations for throughfall precipitation, baseflow, and stormflow at M1

Table 15. Constituent concentrations for throughfall precipitation, baseflow and stormflow at M2

Quantity	Cl ueq/L	NO3-N ueq/L	SO4 ueq/L	NH4-N ueq/L	H ion conc, ueq/L	ICP Na ueq/L	ICP K ueq/L	ICP Mg ueq/L	ICP Ca, ueq/L
TF	16.7	10.1	48.1	8.0	9.0	13.6	46.4	19.8	42.8
Baseflow	11.0	28.1	40.0	0.2	4.5	27.3	11.1	17.4	41.0
Stormflow	8.3	30.6	45.2	0.4	7.5	24.1	12.8	21.5	53.7

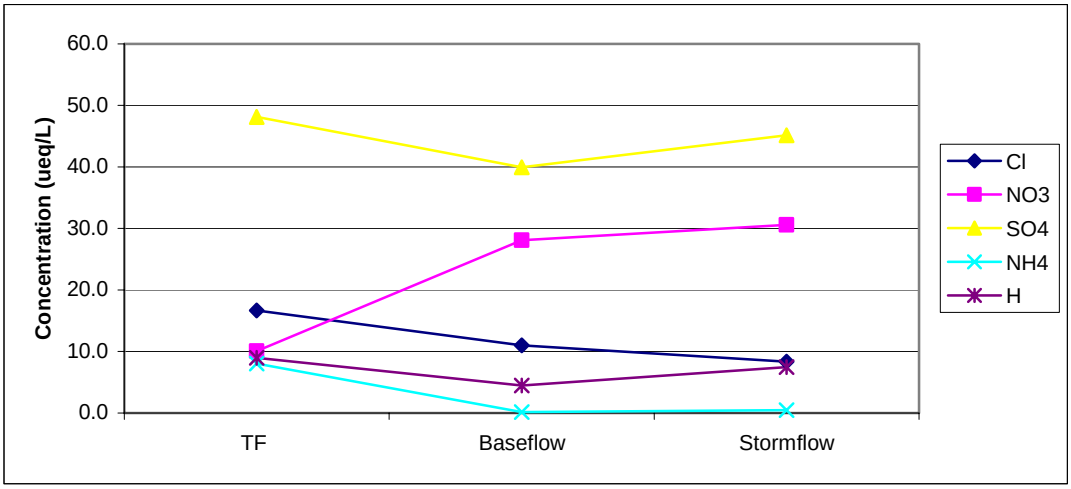

Figure 31. Anion and acid cation concentrations for throughfall precipitation, baseflow, and stormflow at M2

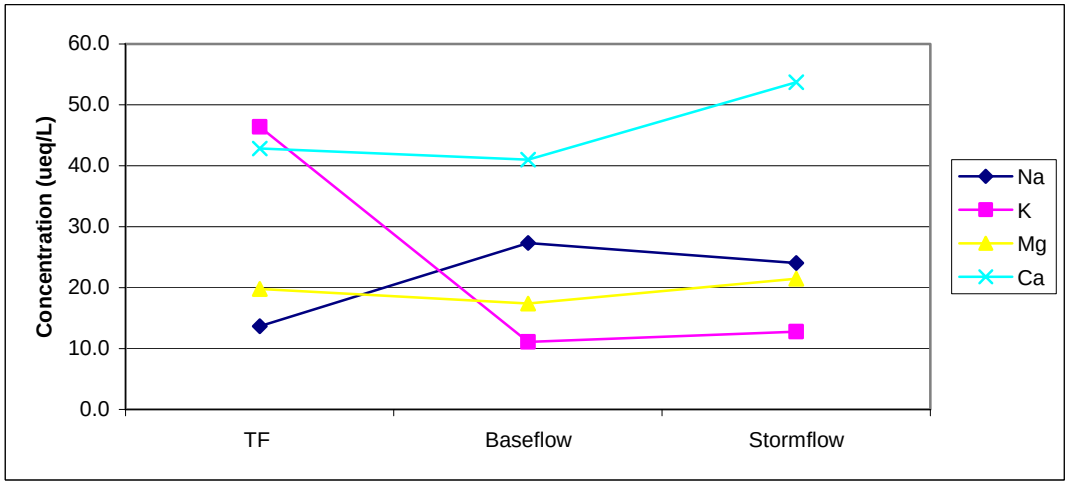

Figure 32. Base cation concentrations for throughfall precipitation, baseflow, and stormflow at M2

Table 16. Constituent concentrations for throughfall precipitation, baseflow and stormflow at M3

Quantity	Cl ueq/L	NO3-N ueq/L	SO4 ueq/L	NH4-N ueq/L	H ion conc, ueq/L	ICP Na ueq/L	ICP K ueq/L	ICP Mg ueq/L	ICP Ca, ueq/L
TF	12.0	22.9	44.4	2.9	7.0	21.7	23.4	19.5	45.8
Baseflow	10.6	46.5	49.2	0.2	5.0	27.3	7.4	29.3	51.1
Stormflow	12.9	53.2	70.9	0.7	21.6	18.8	10.1	35.7	57.3

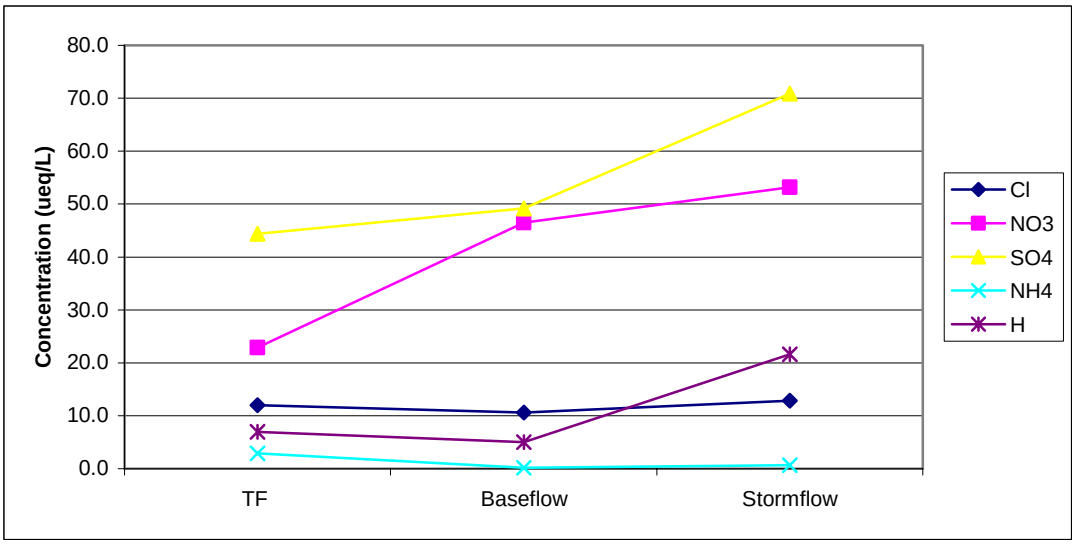

Figure 33. Anion and acid cation concentrations for throughfall precipitation, baseflow, and stormflow at M3

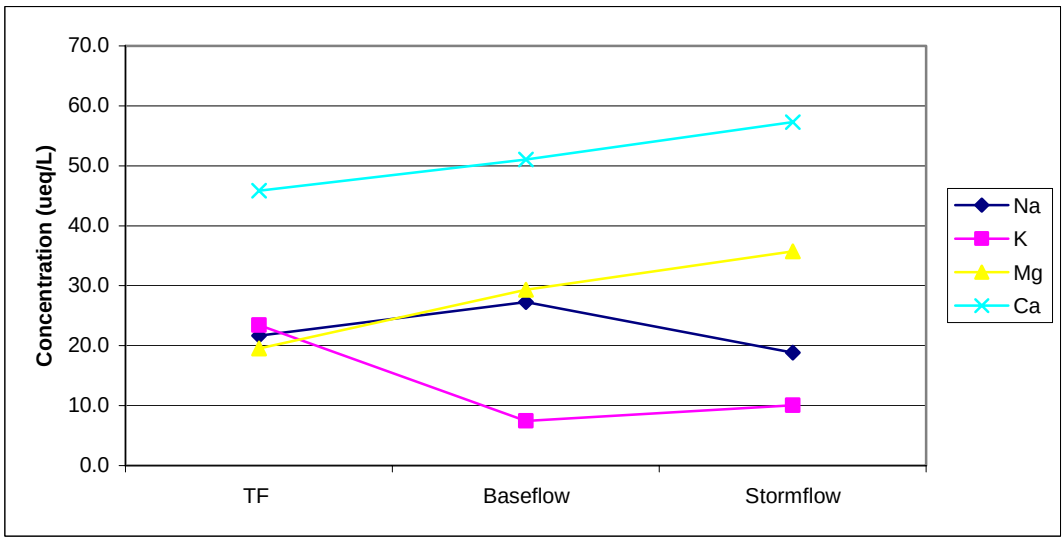

Figure 34. Base cation concentrations for throughfall precipitation, baseflow, and stormflow at M3

Appendix D: Stage-to-Discharge Curves

Stage-to-discharge relationships, or rating curves, were a necessary component of the mass balance analysis. As mentioned in Appendix B, stage-to-discharge measurements were made at an established datum in accordance with USGS Water-Supply Paper 2175. Velocity measurements were made following the Six-Tenths Depth Method, where the average downstream velocity is be assumed to be 0.6 feet below the water surface (WSP 2175). The rating curve for each site is found in Figures 28-30. The semi-log flow vs. depth relationships were found to better predict high and low flows than a polynomial or arithmetic relationship. However, even the semi-log rating curves were found to dramatically over predict high flow at M2 and M3, and slightly-to-moderately over predict flows at M1.

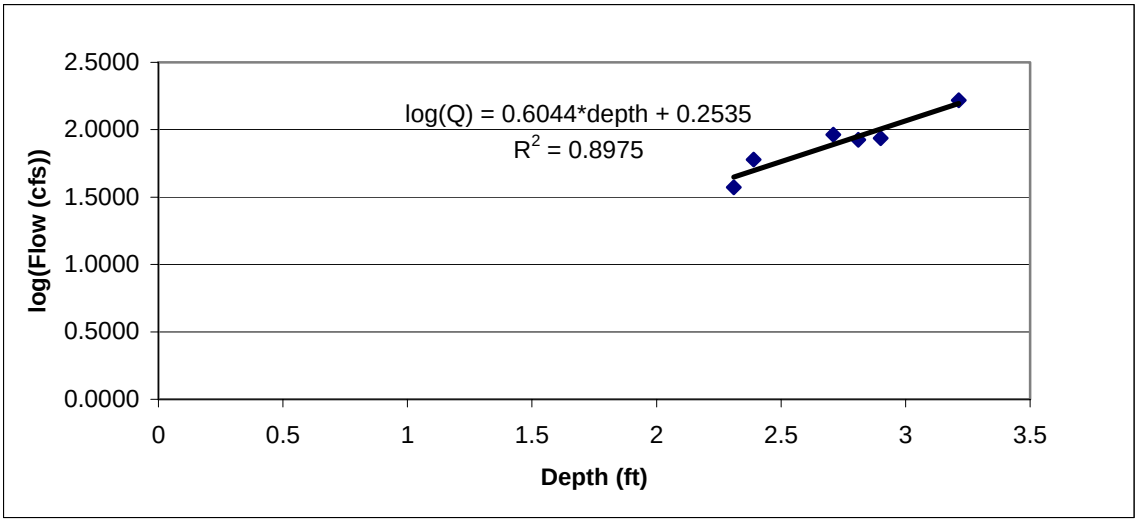

Figure 35. M1 rating curve

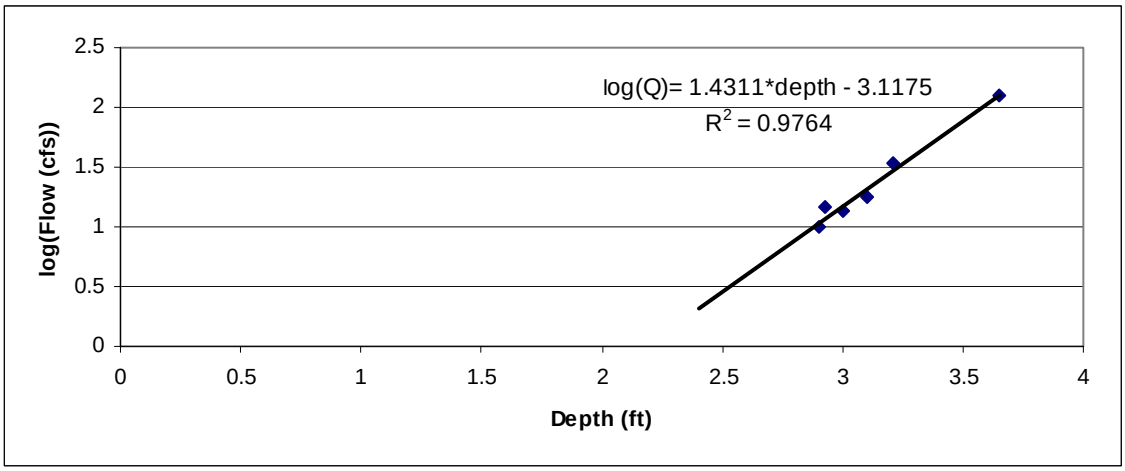

Figure 36. M2 rating curve

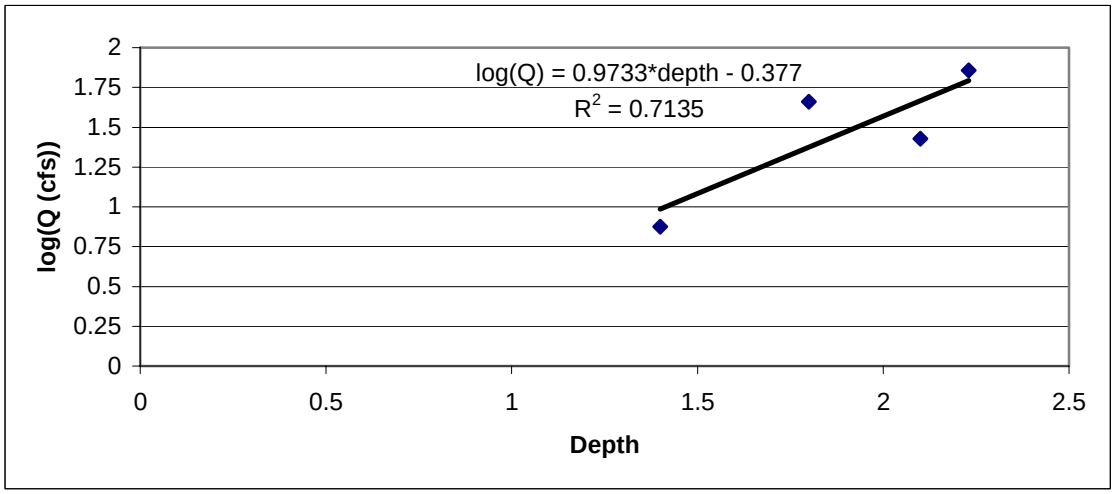

Figure 37. M3 rating curve

Appendix E: Study Sites

Site pictures and geographic coordinates were kindly provided by Keil Neff, a coworker in the MPLP study.

Middle Prong Little Pigeon River
N 35°42.159'
W 83°20.067'
elevation: ~2700 feet

Figure 38. Middle Prong Water Quality Monitoring Site

Figure 39. Middle Prong Sonde

Ramsey Prong
N 35°42.257'
W 83°19.770'
elevation: 2877 ft

Figure 40. Ramsey Prong Water Quality Monitoring Site

Figure 41. Ramsey Prong Sonde

Eagle Rocks Prong
N 35°41.417'
W 83°19.183'
elevation: 3168 feet

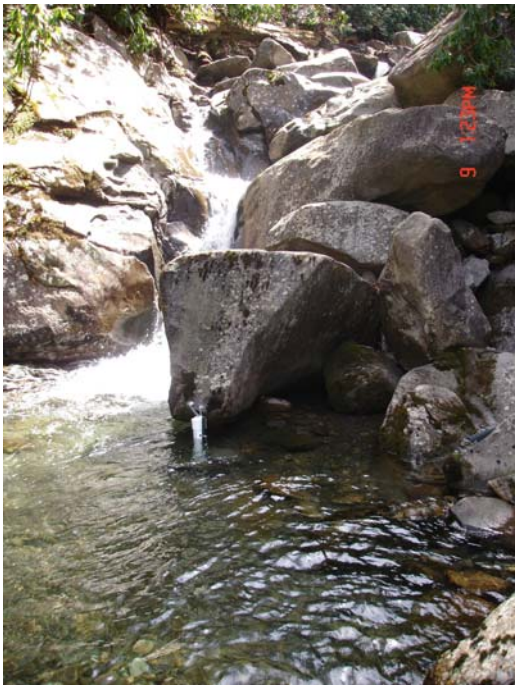

Figure 42. Eagle Rocks Prong Water Quality Monitoring Site

Figure 43. Eagle Rocks Prong Sonde and Trout Cage

Appendix F: Dissolved Organic Carbon Testing

Storm samples were analyzed to determine the dissolved organic carbon (DOC) concentration. Storm samples and blanks were processed by Test America, Analytical Testing Corporation in Nashville, TN. Analysis was done to have an idea of the organic acid concentration, as organic acids are one component of the DOC. Samples were tested from storms on 01/07/07, 03/01/07, and 03/16/07. Results for the respective storms are available in Tables 13-19. DOC concentrations between 1-10 mg/L indicate organic acid concentration is high enough to influence acidity. Streams with DOC greater than 10 mg/L may have organic dominated acidity. The measured stream sample concentrations indicate the streams have low DOC, but may be influenced by organic acidity during storm events.

Table 17. DOC results for M1 on 1/07/07 storm

Sample	DOC conc (mg/L)
M301 @ 4.5 hr	3.19

Table 18. DOC results for M3 on 1/07/07 storm

Sample	DOC conc (mg/L)
M325 @ 4.5 hr	3.28

Table 19. DOC results for M2 on 3/01/07 storm

Sample	DOC conc (mg/L)	Increase (mg/L)	Percent Increase
M353 Baseflow	2.27		
M360 @ 1.5 hr	3.19	0.92	40.5%
M365 @ 5.25 hr	3.67	1.4	61.7%

Table 20. DOC results for M3 on 3/01/07 storm

Sample	DOC conc (mg/L)	Increase (mg/L)	Percent Increase
M355 Baseflow	2.41		
M384 @ 1.5 hr	2.73	0.32	13.3%
M389 @ 5.25 hr	4.71	2.3	95.4%

Table 21. DOC results for M1 on 3/17/07 storm

Sample	DOC conc (mg/L)	Increase (mg/L)	Percent Increase
M413 Baseflow	1.97		
M422 @ 4.5hr	2.23	0.26	13.2%

Table 22. DOC results for M2 on 3/17/07 storm

Sample	DOC conc (mg/L)	Increase (mg/L)	Percent Increase
M414 Bflow	1.54		
M443 @ 6 hr	4.6	3.06	198.7%

Table 23. DOC results for M3 on 3/17/07 storm

Sample	DOC conc (mg/L)	Increase (mg/L)	Percent Increase
M415 Bflow	2.7		
M456 @ 1.5hr	3.23	0.53	19.6%

VITA

Edwin Bradley Deyton was born December 30, 1981, in Knoxville, Tennessee. He graduated from Lenoir City High School, in Tennessee, in May 2000. Mr. Deyton enrolled at the University of Tennessee in August 200 to pursue a Bachelor of Science degree in Civil Engineering. While in college, he worked two semesters as a co-op student employee with the Federal Highway Administration in Sterling, Virginia. Following graduation, Mr. Deyton enrolled in a Masters of Science program at the University of Tennessee where he majored in Environmental Engineering, with an emphasis in Water Resources. Upon completion of his Masters of Science degree, he will begin working as a Civil Engineering consultant in Knoxville, Tennessee. Mr. Deyton is interested in pursuing a Masters in Business Administration degree after several years of consulting work.